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FOREWORD

The widespread interest in and cordial reception given to the published proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications, held at the Massachusetts Institute of Technology in 1937, have led to the publication of the proceedings of the sixth conference. This was held in Cambridge on July 18, 19, and 20, 1938.

The present volume contains, though in somewhat abbreviated form, the thirty-one papers which were presented during the three days of the conference. Space limitations have decreed that not much more than half of the orally presented material be included, but since the condensations have been carried out by the respective authors, little essential material has been neglected. The principal omissions are in the illustrations, which include only the more important selections from a wealth of material exhibited by lantern projection; and the discussions which followed the various papers.

The value of correctly reported discussion is well recognized, but it has not been included here for several reasons. First perhaps comes the difficulty of fairly reporting the sense of a lively discussion. Literal stenographic reports usually carry little but the corpse of verbal interchange, and when such reports are submitted for editing to those responsible they are likely to emerge with little resemblance to the original. Most important, however, appears to be the desirability of preserving the informality and spontaneity of the discussions, and for this a certain degree of privacy is essential. Therefore, the lack of recorded discussion of the sixth conference may be taken as a sacrifice made for the sake of the discussions of a possible seventh.

Many requests have been received for copies of the proceedings of the first four conferences. These have not been published, nor is it probable that they will be, for the rapidity of development of applied spectroscopy is such that constant revision and improvement of methods are necessary.

Some duplication will be found between various papers included herein, but this duplication is thought to be less objectionable than would overzealous meddling from an editor endeavoring to bring a greater degree of coherence and uniformity to the whole. The volume should not be considered as a text or a reference book, but as a compilation of discussions of a rapidly developing field from various aspects.

That applied spectroscopy is in a period of active growth is evidenced by the attendance of more than 250 at the sixth conference, to be compared with 50 who attended the first. Astronomers, biologists, chemists, geologists, metallurgists, physicians, physicists, and industrialists of many kinds find the techniques of spectroscopy of such great advantage that increasingly rapid development of this analytical method seems assured for a number of years to come.

GEORGE R. HARRISON

CAMBRIDGE, MASSACHUSETTS
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PROCEEDINGS OF THE SIXTH SUMMER CONFERENCE ON SPECTROSCOPY AND ITS APPLICATION

THE SPECTROGRAPH AS AN AID IN CRIMINAL INVESTIGATION

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The chemical laboratory serving a police organization is called upon to handle problems of an extremely varied and unusual nature. In the entire field of scientific or industrial research I do not know of any laboratory with which it can be compared in this respect. It is the purpose of this paper to examine the use of the spectrograph in the routine work of such a laboratory; to point out its advantages and to recognize what appear to be its limitations.

The literature records very few instances where spectrographic methods have been employed in police work. In general, those instances that have been reported involve cases in which the material available for analysis was too limited to permit of the usual macrochemical methods. No one who is familiar with the spectrograph can doubt the outstanding advantages of this instrument under these circumstances; but, if such were the only uses, the limited frequency with which these cases occur would scarcely justify the expense involved.

Let us consider the nature of the problems of a police laboratory. The most striking feature is the great variation, both qualitatively and quantitatively, of the material submitted for analysis. In the course of a typical day, one may receive one-half dozen quart jars filled with human organs to be analyzed for small traces of poison, and, from another case, a cold chisel having on its surface an almost invisible amount of a foreign metal. Or, again, one may receive a pair of old trousers with traces of dust on the knees; or paint from a car involved in a hit-and-run accident; or blood stains on a knife; or a pellet of shot removed from a body; or ashes and debris from an incendiary fire; or broken pieces of a burglar's tool; or residues from the scene of an explosion. All these and many others are typical of the so-called routine of a police laboratory. Unusual and varied subject matter requires versatile methods and instruments. In many of these cases spectrographic analysis can be advantageously applied; in a few it is essential.

In addition to the variability of the subject matter, it is generally necessary that these analyses be made as rapidly as possible. The medical examiner who has submitted the organs must have the results of the analysis before he reports the cause of death. The police officer who has submitted the cold chisel may be holding the suspect pending the outcome of the chemical examination. In each of these instances, the spectrograph can shorten the time necessary to arrive at a definite conclusion. In a recent case of vandalism in Massachusetts a quantity of bright red paint had been used. In the course of the investigation by the police officers, several suspects possessing paint similar in appearance were apprehended. In each instance, a brief spectrographic comparison between the paint involved and the paint from the suspect showed that each was of a different origin. Less than an hour was required to arrive at the conclusion. As a result, the investigation could be started along different lines and the suspect in question was saved hours of needless worry. Eventually a sample of paint was submitted which showed no spectrographic or microscopic differences from the paint in question. The suspect possessing this paint at first denied any connection with the offense, but in court pleaded guilty and was sentenced.

The spectrograph is very useful in conducting a qualitative survey of questioned materials. If the results are negative, no further tests are necessary. If, on the other hand, the analysis indicates the presence of elements which would tend to incriminate, further analyses are made by chemical means.

Sometimes the survey spectrogram gives some very interesting and unexpected results. In a recent case, a bottle containing coffee was submitted to be examined for poisons. A wife had accused her husband of attempting to poison her. It was obvious that the brown, ill-smelling sour liquid in the bottle was not pure coffee. A large amount of sulfuric acid was found to be present. No one could possibly drink it. However, the usual spectrographic survey analysis was performed, disclosing considerable traces of copper, lead, and antimony. Since these metals, as well as the acid, were present, the suggestion was given to the investigating officers that possibly the acid could have come from an old storage battery. They again interviewed the wife, found an old storage battery in her house, and accused her of having taken acid from this battery to place in her own coffee. Surprisingly enough, she admitted it. Her object was to obtain grounds for divorce from her husband. The survey spectrogram of the impurities in the acid was more significant than the mere presence of the acid itself.

We have not as yet had the occasion to employ strictly quantitative spectrographic methods in our laboratory. There are several reasons for this. First of all, the materials submitted are too diversified in nature to permit the use of standard procedures. There is no one class of material which would justify the time required to prepare reference standards and develop the necessary technique. Secondly, quantitative methods would be applicable only to materials that were representative, homogeneous, and of sufficient bulk to permit a number of individual spectrograms. In general, such materials are more easily handled by the usual chemical methods. And, finally, we are not always primarily interested in the absolute quantities of a given element; more frequently we wish to know whether the element occurs in the two materials in relatively the same amounts. Our problem is generally one of comparison rather than quantitation.

To illustrate, we may choose a typical case in which spectrographic analysis led to a positive result. During this last winter, a unique accident occurred on one of the large highways near Boston. It was in the early morning, and a thin crust of ice had formed on the concrete road, particularly in the valleys. At the same time, a heavy mist limited visibility to only a few yards. An automobile came over the crest of a hill and stopped in the valley along the side of the road. The driver got out and went toward the back of his car. As he did this, fourteen other cars, in rapid succession, came over the crest of the hill, attempted to stop, and crashed into each other and into the original car. The man who got out of his car was killed. Because of the poor visibility and rapidity of the course of events, no eye witness was able to describe accurately what took place. No one admitted striking the man. Upon examining the clothing of the victim, a small particle of paint was found to be impressed in the fabric near a tear in his overcoat. An examination was made of each of the cars involved in the accident and samples of paint were removed from those automobiles which conceivably could have struck the man. These samples were compared both microscopically and spectrographically with the sample found on the victim. It was seen that in both microscopic features and chemical composition the paint on the overcoat was different from every sample removed from the cars, with one exception; with one paint it agreed perfectly. Because the number of automobiles known to have been in the vicinity, at the time, was limited, it was possible to say, in this case, that this particular car had struck the man.

The chemical examination of bullets and of shot and powder residues is of the greatest importance in the investigation of crimes involving the use of firearms. Various authors have employed the spectrograph as a means to this end. Gerlach and Gerlach have analyzed traces of metal left by a bullet in its course through the tissues of the human body. From five actual cases they find that, as a bullet passes through tissue, traces of the metal are wiped off and that it is possible, by this means, to follow the path made by the bullet through the body by subjecting the various tissues to spectrographic analysis. They concluded that it was possible to distinguish between the entrance and exit wound by the preponderance of heavy metals, particularly lead, present in the former.

In the chemical laboratory of the Massachusetts Department of Public Safety, we have also had occasion to analyze a number of bullet holes. A somewhat different technique from that of Gerlach and Gerlach is used. The apparatus consists of a Bausch and Lomb medium quartz spectrograph and an arc supplied with 110 volts d.c. A small disk is cut from the periphery of the bullet hole in cloth. The fabric is ashed at a low temperature in a muffle furnace and the ash picked up in the cup of a graphite electrode. The sample is arced for 5 seconds.

In all our experiments with bullet holes in clothing, a considerable quantity of lead was detected — and this in spite of the fact that some of the holes were known to have been caused by metal-jacketed bullets. Tin, antimony, and barium were also frequently encountered. The first two elements are constituents of bullet metal, but barium never is. Because both barium and lead are constituents of many primer caps, and because metal-jacketed bullets have no lead or barium on their exterior surfaces, it occurred to us that the primer residue might be a considerable factor in giving rise to those traces around bullet holes. With this

in mind, a number of experiments were undertaken.

We chose for our purposes .32 and .38 caliber revolvers and ammunition. The bullet and powder were removed from each of 96 makes and types of cartridges, representing both black and smokeless powder, old and new ammunition. The primer was then fired into a small cotton plug, and the plug arced in the spectrograph. Small traces of impurities being neglected, the following elements were detected in the various cartridge primers.

ELEMENT	ON PERCENTAGE OF PRIMERS
Antimony	87
Barium	90
Lead	75
Mercury	67
Potassium	31
Manganese	4
Tin	9
Zirconium	1

A typical old-type primer contained antimony, barium, potassium, and mercury. A typical modern primer contained antimony, barium, and lead, with or without mercury. Special high-velocity types also contained considerable tin.

With this information in mind, cartridges were prepared of lead-free primers and metal-jacketed bullets. The purpose was to eliminate lead from the bullet hole. Shots were fired into woolen cloth. To our surprise, lead was still present in considerable quantities around the bullet hole.

During the above experiment, the revolver barrel had not been thoroughly cleaned, so that perhaps the fouling around the lands and grooves of the gun barrel was responsible for the lead in the bullet hole. Accordingly, the barrel was thoroughly cleaned with acid, a wire brush, and clean cotton patches. Shots were again fired, using metal-jacketed bullets, leadless

primers, and a clean gun barrel. Some lead was still present at short distances, although considerably less. Finally, it was found that the only means by which we could completely prevent the appearance of a spectrographically detectable trace of lead around the bullet hole was to prepare special cartridges composed of pure tin bullets, lead-free primers, and powder which had never previously been in a cartridge, and fire the resulting combination from a gun barrel cleaned with acid. With this specially prepared cartridge as a control, shots were fired at various distances, allowing only one factor to vary in each shot. In this way, it was determined that at distances in the vicinity of 3 inches lead was contributed by each factor in the following decreasing amounts: lead bullet > dirty gun barrel > metal-jacketed bullet > lead primer residue. At 1-foot and 6-foot distances only the lead bullet and fouling of the barrel were significant.

In practice we cannot presuppose a clean gun barrel. A series of spectrograms was then prepared, using commercial .38 caliber bullets of various composition, fired in succession without cleaning the barrel, in order to determine whether traces left by the bullet could serve as an indication of its original composition. Lead was found to be present in every case, regardless of the composition of the bullet. Those bullets which contained tin frequently left a detectable trace. Copper did not appear in appreciably greater amounts after the passage of a copper-jacketed bullet than before.

From these results, it can be seen that very great difficulty might be encountered in attempting to determine the chemical composition of the bullet from traces left on the cloth around the bullet hole. The fouling in the gun barrel, left by previous shots, is an uncontrollable complicating fac-

tor. The very presence of lead around every bullet hole is a good indication that that hole is, in fact, a bullet hole and not that caused by some other instrument.

It was interesting to note in these results that barium from the primer was frequently present in the bullet hole, even at 6-foot distances. That this was due to the fouling of the gun barrel by primer residues of previous shots rather than the direct transportation of the particular shot was shown by the following experiment:

A metal-jacketed bullet having barium in the primer was fired at a distance of 6 feet into woolen cloth. The barrel was then fouled with five shots from cartridges of barium primers and lead bullets. Two additional metal-jacketed bullets from cartridges having no barium in the primer were fired into the same cloth. Barium from the primer was absent from the bullet hole of the shot fired through the clean barrel, but present in the hole from the shot through the fouled barrel. The primer components are not transported directly to the bullet hole. They occur as a result of a fouled barrel. This is confirmed by the behavior of potassium from a black powder charge. The original black powder shot showed little or no additional potassium around the bullet hole at a 6-foot distance. But three subsequent smokeless powder shots carried considerable, but decreasing, amounts of potassium to the cloth. Aside from the bullet composition itself, the fouling of the gun barrel is the most important factor influencing residue tests at greater distances.

In conclusion, it may be said that all commercial .38 caliber bullets, regardless of composition, showed lead around the bullet hole when the shot was fired from a fouled barrel at distances of 6 feet or less. At distances of 3 inches the lead around the bullet hole is contributed by four sources of decreasing importance: (1) the bullet; (2) fouling of the gun barrel; (3) lead contamination of the powder, or the base of the jacketed bullet; (4) lead from the primer. At distances of 6 feet the powder and the primer do not directly contribute appreciable amounts of metals to the bullet hole. At this distance only the bullet and the fouling contribute significantly to the metals around the bullet hole.

APPLICATIONS OF THE SPECTROGRAPH TO CRIMINAL INVESTIGATION

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Probably the greatest problem in the police analytical laboratory is the retention of the evidence for courtroom presentation versus the need of this same evidence for purposes of analysis. The spectrograph is of great aid in this connection since but minute quantities of material are needed, and even what is used may not be entirely destroyed. In a recent case, lead pellets in a shotgun homicide which weighed but 65 mg lost only 10 mg during the analysis.

Last fall we were interested in the so-called Close case. Young Morris Close left his mother's home in Albany on the evening of July 19 to go to work in Rochester, and was never again seen alive. A week later, six miles from Kingston City, Missouri, his coat and blanket were found beside the body of an itinerant worker, who had three .38 caliber bullets in his body. Six weeks after Close's disappearance his car was found abandoned in Memphis, Tennessee, with his suitcase in it. On October 9, ten miles east of Rochester a skeleton was found which from dental and other means of identification proved to be that of Close. The skull was sent to the laboratory along with a .38 caliber lead slug found near the remains. The base of the skull had a hole which at first was thought to be a bullet hole, but when scrapings around the hole were tested spectrographically only strong iron lines appeared, and no lead lines. The

supposition is that the hole was made not by a bullet but by some blunt instrument. The bullet found near Rochester and one of those found by the Missouri authorities were tested spectrographically, and found to have the same composition. Incidentally, both were so distorted as to make exact ballistic examination impossible. The murderer of both of these men is believed to be a convict who escaped from a prison near where Close's body was found and who has not as yet been apprehended.

The solution of burglaries also may be aided by means of the spectrograph. In gaining entrance to a barn a burglar used a common pinch bar. A few days later a suspect was picked up with such a tool in his automobile. The marks in the barn door fitted exactly with dimensions of the tool, and careful examination of the bar revealed two very small green smudges similar in color to the paint on the barn door. This tool was sent to the laboratory together with two boards from the door, which showed the tool markings. Some of the paint stain was picked up with ethylene dichloride solvent, and this together with some paint scrapings from the board were tested spectrographically. The scrapings were found to contain not only the barium and chromium of the green stain, but also lead and zinc. Examination of the board then brought out

the fact that there was an undercoat of white paint and the scrapings had picked this up also. When the green was removed from the board with the solvent, the zinc and lead disappeared. Later we secured from the manufacturer of the paint an analysis of the pigment which checked with our results.

Time saved has always been one of the chief points in favor of the spectrograph, and we have found it to be no less true in our investigations. Some meat was sent to the laboratory in a dog-poisoning case, and, while the chemists were making their usual toxicological examination, I ran a spectrogram of the meat, unwashed, just as received. The plate showed barium, and later chemical tests confirmed the finding. This is a rather unusual poisoning, for arsenic, mercury, and strychnine are much more likely to be found. The barium was in the form of the carbonate, which is one of the usual components of rat poisons.

We are now engaged in a series of experiments, the object of which is to determine the elements deposited on cloth through which a bullet has been fired, and the variation in their line density with distance. In other words, do the lead lines, for instance, have a definite decrease in intensity with distance at which the bullet is fired? Our target has been a dummy dressed in undershirt, shirt, and blue serge coat. To date we have experimented only with .32 caliber lead S & W bullets, the coat having been found to contain copper. In near discharge of the weapon (1 inch) the powder constituent manganese was found in addition to lead, copper, arsenic, tin, and antimony. Only lead, copper, and antimony were found at 1-foot, and at 3-feet distance only copper and lead. When copper-free cloth was used it was found that the copper persisted just as strongly as lead. Continuing, shots were fired at 5, 10, 20,

30, 40, and 50 feet. Homicide with a revolver would be unusual at a greater distance than 50 feet. In each case a half-dozen lead lines appeared, though progressively weaker on the shirt and undershirt. Just to see if it were not true that the bullet had only to pass through the cloth regardless of the distance fired, we tried one shot at more than 100 feet. Again the same results appeared, except that the lines were absent in the shirt and undershirt.

It is not the good fortune of the police laboratory to have a spectrum-line photometer; consequently for a quantitative study of the results we had to turn to the General Electric Company. Through the courtesy of Mr. Christian Dantsizen,
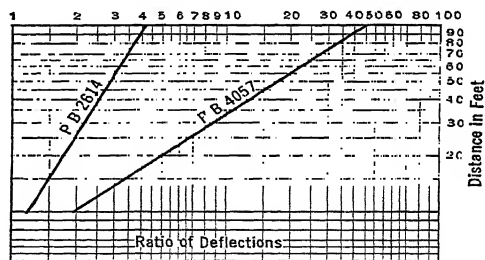
FIG. 1

chief chemist, their spectroscopist, Mrs. Alice P. O'Hara, made the readings, using a Zeiss spectrum-line photometer. The ratio of the readings of the 1 per cent tin internal standard line 2707 A being plotted on log paper against the lead lines 4057 A and 2614 A, the result, as can be seen from Fig. 1, is a straight line. It would be convenient indeed to be able to take a spectrogram of a bullet hole and from it deduce the distance from which the bullet had been fired, but I am inclined to believe from the widely different patterns left on the cloth by the bullet that these results were a happy coincidence and will not be achieved in the future experiments we are planning.

Last October the laboratory received the stomach contents of a young man who had died under mysterious circumstances. He suffered from a gonorrhea phobia and had been having his druggist give him treatments including sulfanilamide tablets. This occurred but a few days before the nationwide prominence given the many deaths from Massengill's Elixir, a preparation containing sulfanilamide mixed with diethylene glycol. While further investigation showed the cause of death to have been Bright's disease, it might be well to explain the process used for the analysis of sulfhemoglobinemia.

The cyanosis which sometimes develops from sulfanilamide therapy is due to the presence of sulfhemoglobin in the blood. Discombe has shown that hydrogen sulfide is formed in the large gut by the action of bacteria on food residues or as the result of administration of elementary sulfur. Under normal conditions, the hydrogen sulfide is partly destroyed by the plasma and is partly excreted by the lungs. However, sulfanilamide seems to act as a catalyst to facilitate the combination of hemoglobin with the sulfide, resulting in sulfhemoglobinemia.

Sulfhemoglobinemia is serious because, like carbon monoxide poisoning, it represents a permanent functional loss of the blood so involved. New hemoglobin must be built to replace it, and this process requires several weeks. Once its presence is discovered the administration of sulfanilamide should be discontinued.

The detection of sulfhemoglobinemia depends on the spectroscope. Sulfhemoglobin has three distinct absorption bands. The first or alpha is narrow and somewhat weak. It is in the red part of the spectrum at about 6180 A. The next or beta band is broader and is very strong. It is in the orange-yellow region in the same position as the alpha band of oxyhemoglobin, at 5780. The third or gamma band is broader but is somewhat weak, and corresponds to the beta band of oxyhemoglobin. Methemoglobin presents a somewhat similar picture in the spectroscope, and careful observation is required to distinguish it from that of sulfhemoglobin. There are again three bands, the only difference being in the position of the alpha band which is at 6300 instead of 6180. If the difference cannot be detected because an accurately calibrated spectroscope is not available, the band in the red of the methemoglobin can be readily destroyed by the addition of a 5 per cent solution of ammonium sulfide. The same band for the sulfhemoglobin will not disappear with the addition of this reagent.

I might say at this point that where the blood sample has been taken after death there is always the danger that the sulfhemoglobin which may appear is merely the result of some putrefaction having occurred before the sample was taken. One runs into difficulty also in the spectroscopic examination of monoxide poisoning, for a blood sample may be such a mixture of oxy and carboxyl hemoglobin that the characteristic bands of carboxyl hemoglobin will not be seen. We have found it more advisable to make our analysis in suspected monoxide poisoning with the Van Slyke apparatus, which is designed for determining the combining power of the plasma, and with which the exact percentage of monoxide can be determined.

In conclusion I should like to tell you of a toxicology case more humorous than tragic. Some years ago in a southwestern state a man whom we shall call John Doe was tried and convicted by a jury, one of whose members we shall call Richard Roe. Time passed, and we find both men working in the same factory in southwestern

New York. Their relations, needless to say, were not pleasant, drawing to a head one noon with the discovery by Richard that the coffee in his thermos bottle had a peculiarly reddish cast and unusually heavy sediment. Richard refrained from drinking the coffee, and, when upon the morrow John seemed surprised to find that he was not at all ill, Richard decided to turn the contents of the thermos bottle over to the state police, where in due time it arrived for analysis.

A toxicological analysis is usually guided by an autopsy report and the finding of the physician who may have been with the patient before he expired. But in this case Richard had not died, in fact, was not even ill. Luck was with us, however, for when the chemists were filtering they noticed that the filtrate turned dark brown within an hour, indicating the presence of some dye or silver salt. Chemical tests for silver proved negative, but Millon reagent showed protein present. This indicated the presence of a weak solution of organic silver salt used in the treatment of gonorrhea. A teletype request to the inspector in charge inquiring whether the suspect had purchased any Protargol (silver proteinate) brought the reply that he had purchased a small quantity of $\frac{1}{2}$ per cent Protargol solution from a local drugstore. Experimental solutions were made of the same type, and it was found that he could not have added more than 30 cc per 500 cc of coffee. Since Protargol contains only 8 per cent of silver and the final solution could not contain more than 0.012 gram of silver, which was entirely too minute an amount for the average chemical test, the coffee sediment was then tested spectrographically and silver was found to be present.

The legal aspects of the case presented quite a problem, for the presence of a small quantity of organic silver could not be termed " poison or a destructive or noxious thing." Upon the suspect's being questioned he stated that he had a strong desire to infect the ex-juror with gonorrhea, with which he was suffering. To his perverted mentality the giving of the drug for the treatment of gonorrhea to a healthy person would of itself induce the disease.

SPECTROSCOPIC DETECTION OF RARE EARTHS IN PLANTS

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The spectrographic laboratory handling general analytical work is frequently called upon to solve problems which arise in the course of ordinary chemical analysis. Such problems include survey analyses of complex samples preliminary to chemical analysis, the testing of completeness of chemical separations, and the identification of unknown materials. A considerable part of the spectrographic testing done at the National Bureau of Standards involves the solution of these problems.

An interesting example of the value of spectrographic analysis was encountered recently in the examination of a material separated from plant ash. Mr. W. O. Robinson, of the Bureau of Chemistry and Soils of the United States Department of Agriculture, has been engaged in the chemical determination of the elements present in plant materials. It was established in his laboratory that the air-dried leaves of the hickory and sweetleaf may contain as much as 1.5 and 6.5 per cent of crude alumina, respectively. The abnormal behavior of the crude alumina precipitate obtained from the hickory leaves from a tree growing on a pegmatite vein in Amelia, Virginia, led to the separation of a concentrate of a group of oxides amounting to 0.2 per cent of the dry weight of the leaf. The appearance and behavior of this sample indicated that it was a mixture of rare earths. Since the chemical identification of the rare earths is extremely laborious, involving time-consuming separations, the spectrograph remains practically the only tool for rapid identification. Our laboratory was asked to test the concentrates, and two samples were subjected to the examination for 64 elements, including the rare earths, which constitutes our routine survey analysis. The samples were found to consist of a mixture of rare earths nearly free of the common elements.[1]

The method used for tests of this character is as follows: Portions of the samples are burned in both carbon and copper arcs, and the spectra are photographed with a grating spectrograph. This instrument has proved, over a period of years, to be very convenient both for qualitative and quantitative work.

The concave grating of 15,000 lines to the inch and 21-foot radius of curvature is mounted in parallel light as described by Meggers and Burns.[2] The images are stigmatic, making it possible to use a diaphragm at the slit to permit photographing the spectra of twelve samples without moving the plate holder. The plate holder is made of two parallel rails bent to fit the focus and of a length such that three 10-inch plates may be accommodated. Usually two Eastman 33 plates are exposed, covering the range between 2400 and 4800 A in

the first order with a dispersion of 5.2 A per millimeter. After processing, the dry plates are examined with a microscope on the stage of a micrometer comparator. The plate is adjusted on the stage in a position such that by turning the micrometer head to predetermined settings the plate may be checked rapidly and with certainty for the sensitive lines of the elements. Estimated intensities are recorded for the lines of the elements found, and semiquantitative results are reported for the analyses. On the basis of general experience, or preferably, on comparison with standards, the elements are listed according to their concentrations

uniform high dispersion. A portion of a typical set of exposures of rare-earth concentrates is shown in Fig. 1.

The complexity of the spectra of these concentrates is evident. The individual elements may have several thousand lines in their spectra, and a mixture of ten or eleven such elements can produce quite a complicated plate. The definition of the lines and the sharpness of the cut-off at the ends of the lines due to the stigmatic property of the grating mounting are clearly shown.

Examination of the plates showed that eleven rare-earth elements were present in the concentrates. Ce, La, Y, Pr, and Nd

Fig. 1. Arc Spectra in the Region 3900–4180 A. 1. Iron. 2. Copper + rare-earth concentrate from mineral source. 3. Copper + rare-earth concentrate from mineral source. 4. Copper + rare-earth concentrate from hickory leaves through fluoride separation. 5. Copper + rare-earth concentrate from hickory leaves through oxalate separation. 6. Copper.

in the samples, using the scale: " Major constituents," more than 0.5 per cent; "minor constituents," between 0.01 and 0.5 per cent; and "traces," less than 0.01 per cent. A finer gradation is also employed in which the elements are designated: "Strong," more than 1.0 per cent; "moderate," 0.1 to 1.0 per cent; " weak," 0.01 to 0.1 per cent; and " trace," less than 0.01 per cent. In many cases this report gives sufficient information to the analyst, but if necessary it may be followed by quantitative determinations.

There is a real advantage in using the grating spectrograph for tests of this type since, with one exposure, more than 2400 A of the spectrum may be obtained with a

made up the bulk of the material, with smaller amounts of Sm, Eu, Gd, and Yb, and traces of Dy and Er.

The large amount of concentrate obtained from the hickory leaves indicated that the rare earths might be detected in the original ash of the leaves. This was examined, and in addition to nineteen common elements, nine rare-earth elements were detected. Of the group of rare earths previously found, Dy and Er were not detected. It is interesting to note that Sc was not found in this hickory leaf.

A concentration of rare earths of 0.2 per cent of the dry weight of the leaf is rather large. It equals the concentration of SiO_2 in the sample and exceeds the MnO at 0.149

per cent and the Na_2O, which is 0.02 per cent.

Examination of the literature shows that the detection of rare earths as a group in plant materials has been reported. Mellor[3] states that Crookes and Cossa found rare earths in rice and tobacco ash and also in human bones. Tschermak found 10 per cent total rare earths in an ash of coal from Kutais Caucasus and smaller quantities in the ash of several plants.

A recent paper by Drobkov[4] indicates that small amounts of rare earths may have a pronounced effect on plant growth. Increased yields of 291 per cent in the weights of pea pods were attributed to the presence of rare earths in the culture medium in which the plants were grown.

The rare earths may be available to the plant through the phosphatic fertilizers as well as in the soil itself. Drobkov states that phosphorites contain 0.05 to 0.8 per cent rare earths, and bone meal sometimes as much as 0.8 per cent. Clarke and Washington estimate that the earth's crust contains 0.02 per cent yttrium and cerium earths, so that it is evident that the rare earths are not quite so rare as is generally believed.

Because of the possible influence of the rare earths on the plant, it appeared worth while to us to examine further into the occurrence of these elements in plants. Up to the present time the ashes of the leafy portions of the following plants have been examined: hickory, sweetleaf, soy bean,

TABLE I

DATA ON RARE EARTHS IN PLANT MATERIALS

(The figure given for the rare-earth concentrate is the percentage by weight, with respect to the dry weight of the plant material.)

Source	Hickory Leaves Rockville, Md.	Hickory Leaves Hagerstown, Md.	Hickory Leaves Amelia, Va.	Hickory Leaves Atkinson, N. C.	Black Raspberries Amelia, Va.	Gray Birch Leaves Norway, Me.	Sweetleaf Raleigh, N. C.
Amount of rare-earth concentrate	0.17%	0.03%	0.20%	0.009%	0.016%	0.008%	0.029%
Sc	Trace	Trace	....	Trace	Trace	Trace	Moderate
Y	Strong	Strong	Strong	Strong	Weak	Weak	Moderate
La	Strong	Strong	Strong	Strong	Trace	Trace	Weak
Ce	Strong	Strong	Strong	Strong	Trace	Trace	Weak
Pr	Moderate	Weak	Weak	Weak	.....	.....	Trace
Nd	Strong	Strong	Strong	Strong	.....	.....	Weak
Sm	Moderate	Weak	Weak	Weak	.....	.....	Trace
Eu	Moderate	Weak	Moderate	Moderate	.....	.....	Weak
Gd	Moderate	Weak	Weak	Weak	.....	.....	Trace
Tb	Trace	.....	....	....	.....	.....	....
Dy	Weak	Weak	Weak	Weak	.....	.....	....
Er	Moderate	Weak	Weak	Weak	.....	.....	Trace
Yb	Moderate	Weak	Weak	Weak	.....	.....	Trace

wheat, ragweed, and grapevine from different localities. Rare earths were detected in only one sample in the direct examination, that being the hickory growing near a pegmatite vein. However, after chemical concentration had been applied to birch and sweetleaf ashes, rare earths were identified. In the sweetleaf eleven rare earths were found, as follows: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Er, and Yb; whereas in the birch leaves and in a sample of black raspberries only Sc, Y, La, and Ce were found. In no sample yet examined have Ho, Tm, and Lu been found, but there is no reason to believe that they are absent; they are probably below the range of sensitivity. These are the rarest of the group of rare earths. The spectrum of illinium, element 61, is not known, and therefore its possible presence in the samples could not be checked.

The results of the examination of samples of rare-earth concentrates from plants from several sources are given in Table I. The concentrates from the hickory leaves were found to consist mainly of rare earths, but the concentrates from the black raspberries, gray birch leaves, and sweetleaf contained considerable amounts of common elements.

It is planned, in cooperation with the Bureau of Chemistry and Soils, to supplement this report of the presence of rare earths in plants by a survey of additional samples and quantitative determinations in representative cases. The recognition of the occurrence of small amounts of this group of elements in plants is perhaps of only academic interest at present, but in view of the effects of certain rare constituents, such as boron, on plant growth, the possibility of modification of growth characteristics by the rare earths should not be overlooked.

REFERENCES

1. W. O. ROBINSON, R. WHETSTONE, and B. F. SCRIBNER, *Science,* 87, 470 (May 20, 1938).
2. W. F. MEGGERS and K. BURNS, *Sci. Papers Natl. Bur. Standards,* 18, 185 (1922), S441.
3. J. W. MELLOR, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," V, Pt. 1, p. 531.
4. A. A. DROBKOV, *Compt. rend. Accad. Sci. U.R.S.S.,* 17, 265–7 (1937) (in English).

SIMULTANEOUS QUANTITATIVE DETERMINATION OF SEVEN ELEMENTS IN GRASSES AND LEGUMES SPECTROGRAPHICALLY

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In August, 1928, an agronomic program involving the study of eighteen different kinds of grasses and legumes was started at Beltsville, Maryland, in cooperation with the Bureau of Animal Industry. The work was carried on for five years through the season of 1933, but was seriously hindered by eighteen months of deficient rainfall in the fall of 1929, and in 1930. The effects of the addition of nitrogen, potassium, and phosphorus, alone and in various combinations, on yields and chemical composition at various times during the growing seasons were studied. Analyses were made for percentages of ash, calcium, phosphorus, ether extract, crude fiber, crude protein, and albuminoid nitrogen.*

At the time the samples were collected, no thought of spectrographic analysis controlled the technique used so that the method was one customary for ordinary chemical analysis. The herbage was harvested with a lawnmower whenever the

*Papers which have previously been published on this are: H. L. Wilkins and H. N. Vinall, "The Effect of Lime and Certain Fertilizer Constituents on the Yield and Composition of the Herbage from Pasture Plots at Beltsville, Maryland," *J. Am. Soc. Agron.*, 25 (No. 9), 603–611 (September, 1933); Vinall and Wilkins, "The Effect of Fertilizer Applications on the Composition of Grasses," *ibid.*, 28 (No. 7), 562–569 (July, 1936).

growth reached a height of 4 to 5 inches. After being weighed to measure yield, random samples were taken for chemical analysis. They were ground in a large Wiley mill which had exposed parts of brass, particularly the screen at the bottom perforated with holes 1.0 mm in diameter. The air-dried material was stored in glass-topped Mason jars.

When the facilities of a spectrographic laboratory became available, these samples offered an excellent opportunity for an exploratory analysis of the relative amounts of elements accumulated by grasses and legumes which vary widely in physiological behavior. Accordingly, samples taken during the growing seasons of 1931 and 1933 were analyzed for Mg, Mn, Al, Cu, Fe, K, and Ca by a technique which permits their rapid simultaneous determination, using a large spectrograph of the Littrow type.

We have found that wandering of the arc, which has given trouble to a number of investigators in the past, may be entirely prevented. When electrodes whose diameter is 6 mm or more are used, the wall of the cylinder, drilled in one end of the electrodes to contain the samples, is turned down to a sufficient degree of thinness. By this means the current density was such that a very steady arc was pro-

duced. The same result can, of course, be secured by using a lower electrode whose diameter is less than 6 mm. If a relatively large amount of a salt such as KCl or NaCl is being volatilized, the arc wanders badly, but with a sample equivalent to approximately 1 mg of ash, such as was used in this work, no trouble was encountered. Evenness of burning of the lower electrodes was increased by pointing the upper electrode to needle sharpness in a pencil-sharpener. The drilled cavity was 3/16 inch in depth and 1/4 inch in diameter. These dimensions are based on principles discussed in a study made by Chaney, Hamister, and Glass[1] of the properties of carbon at arc temperature.

Duffendack's suggestion, made at the Fourth Spectroscopy Conference, has been adopted. All electrodes have been pretreated with kerosene before the addition of any solution to prevent dissolved salts from soaking down into the electrodes.

Maintenance of a constant interelectrode distance is an important factor in securing precision. We have found that blackening of the spectral lines used increases with increasing interelectrode distance up to 4 to 5 mm. In this region the rate of change seems to be at a minimum. With further separation, blackening decreases. Although an interelectrode distance of 4 to 5 mm might have been more desirable from the standpoint of precision, an arc length of 1.0 mm was used in order to decrease line blackening. In this connection, Milbourne[2] claimed that a distance of 1.0 mm aided in securing reproducibility under the conditions of his set-up.

The ash content of our samples was such that a charge of 10 mg dry weight for the grasses and 6 to 8 mg for the legumes, in connection with the optical system used, gave lines whose blackening was suitable for measurement. The charges were either weighed in the electrodes or were transferred to the electrodes without appreciable loss, and were then ashed in a muffle furnace whose maximum temperature was 450° C. On cooling, kerosene was added to the ash, followed by 1 : 4 HCl to convert oxides and carbonates to chlorides. After drying at 90° C the charges were ready for burning in the arc.

A current of 14.5 amperes and 140 volts was used to shorten the time required for complete burning of the charge, also because the work of Duffendack, Wolfe, and Smith[3] suggested that above 12 amperes there was a minimum rate of change of blackening with amperage.

The short slit length of 1.0 mm permitted us to secure 64 spectra on a plate. These consisted of 18 spectra of the standard, 6 dilutions in triplicate, and spectra of 23 samples in duplicate.

A slit width of 50 microns, the selection of a sensitive plate (Eastman Type II-B), and a high amperage made it necessary to counterbalance the relatively great line blackening which otherwise would have resulted. Accordingly, no condensing lens was used, and the light was cut down by means of a rotating sector disk with a 7.8 per cent opening. As mentioned before, a small charge and a short interelectrode distance were used. We exposed until all the charge was burned off (60-90 seconds), guided by exploratory moving-plate studies and by observation of each charge as it was being vaporized.

The plates were not calibrated, and we did not use internal standards.

The make-up of our stock standard solution was based on the analysis of a sample of Kentucky blue grass. The composition of this solution was as follows (Micrograms per 0.1-1 ml) : Ca, 180.7;

Mg, 83.5; Al, 27.0; Fe, 27.3; Cu, 1.7; Ba, 4.1; K, 782.0; Na, 46.0; P, 129.1; Mn, 4.3; and B, 11.8. Dilutions were made with 1 : 10 HCl until a tenfold dilution was reached. Pipets graduated in 0.001 ml were used to measure 0.1-ml amounts of the various dilutions into electrode cavities pretreated with kerosene.

A Bausch and Lomb non-recording densitometer was used to read the plates. At the suggestion of Scribner,[4] an iris diaphragm was mounted above the projection unit for control of sensitivity. At his further suggestion, the metal plate carrying the slit and the photronic cell was placed in a horizontal position in front and at the base of the densitometer. Galvanometer deflections plotted against the logarithm of the concentration expressed in micrograms gave curves which were linear over most of the concentration range.

The following wavelengths were chosen for measurement: Mg, 2780; Mn, 2801; Ca, 3006; Al, 3082; Cu, 3247; Na, 3302; Fe, 3441; and K, 3446. Later work indicated that the manganese line at 2795 gave results which were about 15 per cent lower, and checked better with chemical determinations for manganese.

The plates were developed in Eastman D 11 developer at 18° C for 5 minutes.

In all, 436 samples have been analyzed in duplicate. In addition, more than 200 samples have been reanalyzed. Precision has been measured by averaging the percentage deviations from the means of all these sets of duplicate analyses. With the exception of Cu, the average of hundreds of deviations from the means of duplicate samples was less than 10 per cent for K, Mg, Al, Fe, Ca, and Mn. The precision figures for the latter part of the work were all less than 10 per cent, owing to improved technique.

A series of five runs on as many plates using sample 1229 averaged 10 per cent or less except in the cases of Al, Cu, and Fe, where the average percentage deviation from the mean was respectively 12.5, 15.0, and 16.0. Substantially the same results were obtained when some 34 samples representing 13 different kinds of grasses and legumes were rerun on two or more plates.

No doubt, precision could have been materially improved by plate calibration, by finer grinding of the samples, and by use of a larger charge in combination with a slower plate. Factors which affect the way in which dissolved charges dry down on the electrodes seem to be an important cause of variation. Apparently there is a marked difference in blackening, depending on whether the salt deposit is half way or all the way up the sides of the cavity, although position of the deposit in the electrode does not seem to be the only factor involved. Potassium chloride is by far the most abundant constituent of plant ash treated with hydrochloric acid, and potassium chloride is notorious for creeping when its concentrated solutions are evaporated. Preliminary work indicates that, in order to secure residues which dry down from solution reproducibly, the substitution of phosphoric acid for hydrochloric acid would be more satisfactory.

Accuracy tests have not been completed. At present we have data comparing percentages of calcium secured by chemical and spectrographic methods, shown in Table I, and comparisons between chemical and spectrographic values for a number of elements for one sample of Kentucky blue grass, shown in Table II. We are indebted to Dr. R. E. Davis, of the Bureau of Animal Industry, for the calcium analyses.

In the case of calcium there is useful

agreement for the different kinds of samples with the exception of timothy. This may be owing to structural peculiarities

TABLE I

SPECTROGRAPHIC VS. CHEMICAL VALUES: PERCENTAGE CALCIUM

Grass or Legume*	Number of Samples	Chemical Average	Spectroscopical Average	% Deviation from Mean
Kentucky blue	5	0.42	0.36	8.4
Red top	10	0.67	0.58	7.1
German bent	16	0.59	0.55	3.0
Perennial rye	8	0.54	0.48	5.9
Timothy	15	0.47	0.31	20.6
Alfalfa*	2	1.33	1.18	6.0
Alsike clover*	1	1.80	1.60	5.9
White clover*	37	1.42	1.27	5.9

which make it difficult to sample unless it is very finely ground. The precision for all classes of samples was excellent, varying from 3 to 7 per cent. The use of line 3181 gave much less satisfactory results than line 3006; the results in general were much lower.

As a control on technique, especially the preparation of the standard, sample 1229 was repeated on every plate. The spectrographic averages for the different elements are tabulated in comparison with the chemical averages. Most of the chemical methods used were colorimetric. The reagents were "Aluminon" for Al, sodium diethyldithiocarbamate for Cu, thioglycollic acid for Fe, chloroplatinic acid for K, and periodate for Mn. The only gravimetric methods used were the uranyl zinc acetate method for Na and the pyrophosphate method for Mg.

None of the differences between the spectrographic values and the chemical values is statistically significant except in the case of Na. We do not know the reason for the low spectrographic value for Na, unless it was the ratio of K to Na in the standard. Higher values for Na may be obtained by altering the K to Na ratio, but under such circumstances other elements are thrown out of line. The present standard represents the sixteenth in a series of tests and is a compromise.

There was considerable deviation since older values were included before full control of some of the analytical variables was obtained. The precision, expressed as

TABLE II

SPECTROGRAPHIC VS. CHEMICAL VALUES: KENTUCKY BLUE GRASS 1229

Element	No. Plates	Spectroscopic Average	Chemical Average	% Deviation from Mean
Mg	30	0.22	0.237	3.5
Mn	29	0.018	0.015	9.1
Al	30	0.078	0.090	7.1
Cu	30	0.0058	0.0050	7.4
Na	24	0.084	0.154	29.4
Fe	30	0.080	0.084	2.4
K	30	3.3	2.6	8.5

NOTE: Chemical values for Fe and Cu have been corrected for the amounts remaining unextracted in the silicious residue of the ash by spectrographic analysis of the ash. Uncorrected values: Fe — 0.061 Cu — 0.0045.

coefficients of variation, ranged from 17 to 26 per cent. In percentage average deviation from the mean for the last 14 plates, the precision ranged from 5.5 per cent for Na to 11.1 per cent for Al. The concordance with the chemical values seems to indicate that analytical errors are

symmetrically distributed about a true mean.

In spite of the fact that relatively small amounts of ash were used in the chemical analyses and that the silicious residues were thoroughly extracted, spectrographic analyses showed them to be impure owing to the unextracted elements. Analysis of the residues and subsequent corrections raised the percentage of Fe from 0.061 to 0.084 and the percentage of Cu from 0.0045 to 0.0050. The Mn in the residue has not been measured, otherwise there probably would have been closer agreement; the reverse is true of Al. Comparison of the data for Mg is interesting, for the chemical method, the "official method" for the A.O.A.C., is said to give slightly high results.

Rusoff, Rogers, and Gaddum[5] have compiled a table showing results secured by various investigators on the copper content of forage grasses. The average of these results is about 7 parts per million, whereas in our work 50 parts per million is a typical value. Our high values may result in part from soil contamination of the samples as well as from the Wiley mill. That contamination from these sources has not seriously affected our Cu determinations is indicated by the work of Green and Goldsworthy.[6] They found that the Cu content of unsprayed leaves of Kieffer pear trees grown in Beltsville soil in 1936 averaged about 0.56 microgram per square centimeter. The average weight was 8 mg per square centimeter, according to the authors' personal communication; the Cu concentration then becomes 69 parts per million. Their samples were unground and relatively free from soil contamination. That plants can accumulate large quantities of Cu is shown by the work of Bateman and Wells,[7] who found that various plants growing in a copper-tailing region contained amounts of Cu ranging from 46 to 621 parts per million.

This table and the next one summarize the spectrographic values for the different grasses and legumes. As noted before, 436 samples have been analyzed, so that these short tables represent a considerable concentration of the data.

The purpose of these tables is to show the levels of concentration of the various elements. Nothing can be said at present concerning the effects of date of cutting or combination of fertilizer on the concentration of the elements, as the data have not yet been analyzed statistically. The figures may be characterized as " background data " since interpretation and application must await similar analyses made on like plants grown on other soils and under different climatic complexes. For example, German bent grass apparently contained the highest percentage of Mn. Is this invariably true, and is the property of accumulating a high content of Mn an inherited characteristic? Clearly, many comparative analyses must be made under many sets of environmental conditions to answer these questions.

The data of Table III indicate the following ranges of concentration: Mg, 0.17 to 0.42 per cent; Mn, 0.017 to 0.054 per cent; and K, 1.7 to 5.1 per cent. The bulk of the ash consists of Si and K; Mg is present in about ten times the concentration of Mn.

The figures for Cu show a range from 30 to 80 parts per million. The ratio between maximum and minimum values is much greater for Al (0.03 to 0.19 per cent) and Fe (0.04 to 0.19 per cent) than for the other elements.

This may be explained on a basis of soil contamination of the samples. In cases of apparently gross soil contamination, characterized naturally enough by

maximum ash content, the greatest effect is on the concentrations of Fe and Al. Soil contamination is almost certainly present in red top samples collected in 1931.

ful in the simultaneous analysis of forage grasses for the following elements: Ca, Mg, K, Mn, Cu, Fe, and Al.

TABLE III

SUMMARY OF SPECTROGRAPHIC ANALYSES

Grass or Legume *	Mg		Mn		K		Al		Fe		Cu	
	1931	1933	1931	1933	1931	1933	1931	1933	1931	1933	1931	1933
Kentucky blue	0.23	0.22	0.022	0.022	2.6	2.9	0.06	0.07	0.05	0.05	57	50
Tall oat	0.35	0.20	0.031	0.028	3.7	4.4	0.12	0.08	0.11	0.08	50	33
Meadow fescue	0.34	0.32	0.027	0.033	3.6	3.2	0.09	0.10	0.09	0.11	46	30
Red fescue	0.21	0.20	0.034	0.042	2.1	3.4	0.04	0.07	0.07	0.06	39	43
German bent	0.23	0.25	0.050	0.054	3.6	3.2	0.09	0.07	0.11	0.07	47	52
Red top	0.28	0.23	0.033	0.031	3.2	3.0	0.15	0.06	0.15	0.05	40	48
Brome	0.23	0.26	0.041	0.031	3.8	5.1	0.14	0.12	0.16	0.11	55	89
Reed canary	0.27	0.17	0.032	0.023	3.2	3.0	0.13	0.03	0.13	0.02	47	31
Canada blue	0.17	0.17	0.017	0.018	2.5	2.8	0.07	0.05	0.06	0.05	45	57
Italian rye	0.34	0.25	0.035	0.036	3.5	3.6	0.15	0.11	0.17	0.10	44	40
Timothy	....	0.21	....	0.026	...	3.4	....	0.04	....	0.04	..	57
Perennial rye	0.37	0.27	0.042	0.041	3.6	2.8	0.16	0.17	0.18	0.18	57	42
Orchard	0.28	0.32	0.039	0.044	4.7	4.2	0.10	0.07	0.12	0.06	43	76
Red clover *	0.42	....	0.034	.....	2.4	...	0.19	....	0.17	....	58	..
White clover *	0.35	0.26	0.025	0.020	3.2	2.7	0.11	0.09	0.08	0.06	54	40
Alfalfa *	0.30	....	0.028	.....	3.5	...	0.16	....	0.19	....	44	..
K. lespedeza *	0.27	0.24	0.026	0.027	2.2	1.7	0.11	0.10	0.10	0.08	42	33
Alsike clover *	0.38	0.32	0.030	0.024	3.3	2.8	0.14	0.08	0.16	0.05	64	39

All calculations were made on a dry-weight basis.

The average ash content of these samples was 17 per cent in 1931 and 12 per cent in 1933. The increase of 5 per cent in the ash content is reflected by large increases in the percentages of Fe and Al, while the other elements are unaffected, with the possible exception of Mg. Other examples are reed canary grass, Italian rye, and alsike clover samples, all collected in 1931.

In conclusion, the spectrographic technique described here has sufficient precision, accuracy, and speed to be very use-

REFERENCES

1. CHANEY, HAMISTER, and GLASS, *Trans Electrochem. Soc.*, 67 (1935). Preprint.
2. MILBOURNE, *J. Soc. Chem. Ind.*, 56: 205 T (1937).
3. DUFFENDACK, WOLFE, and SMITH, *J. Ind. Eng. Chem., Anal. Ed.*, 5, 226 (1933).
4. SCRIBNER, *Proc. Fifth Spectroscopy Conference*, p. 54 (1937).
5. RUSOFF, ROGERS, and GADDUM, *J. Agr. Research*, 55, 733 (1937).
6. GREEN and GOLDSWORTHY, *Phytopathology*, 27, 957 (1937).
7. BATEMAN and WELLS, *J. Am. Chem. Soc.*, 39, 811 (1917).

SPECTROSCOPIC METHODS OF VITAMIN MEASUREMENT

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The use of ultraviolet absorption spectra for the identification and quantitative assay of the vitamins has been known for many years. The discovery and investigation of the properties of each of the vitamins have been accompanied by the measurement of its ultraviolet absorption spectra and the attempt to set up a quantitative correlation between the intensity of the absorption maxima and the biological potency of the vitamins. This correlation has been so successful in respect to vitamin A, and the results are commercially so important, that it seems worth while to limit the present discussion to some of the spectrographic methods for vitamin A determination.
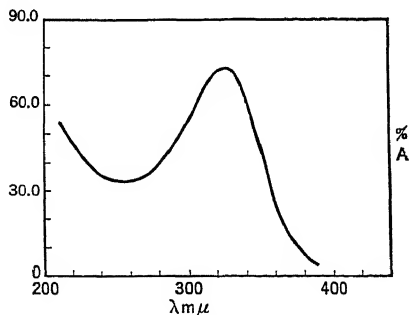

Fig. 1

The absorption spectrum of a solution of vitamin A concentrate in absolute alcohol is shown in Fig. 1. In using the 3280 A absorption band as a means for quantitative vitamin A assay it is necessary, however, to make allowances for the possible presence of extraneous absorbing materials — the so-called ultraviolet dirt. So far as rich concentrates — sturgeon and halibut-liver oils — are concerned the contribution to the gross absorption at 3280 A of constituents other than vitamin A is negligible. But for cod-liver oils the non-vitamin A absorption at 3280 A is relatively very much greater, the amount depending upon such factors as color and free fatty acid content. Since it has been found that the non-saponifiable extracts are usually free from extraneously absorbing material at 3280 A this source of error may be readily avoided. Considerable care must be taken, however, that no loss of vitamin content occurs during the preparation of the extract.

All the spectrographic methods for determining vitamin A concentrations depend upon the photometric measurement of the absorption of radiation by vitamin A oil solutions in the vicinity of the 3280 A absorption peak. They differ in the method whereby essentially monochromatic radiation near the 3280 A absorption peak is obtained, and the method of measuring the intensity of the unabsorbed portion of this radiation. Essentially monochromatic radiation of approximately 3280 A wavelength may be obtained in one of two ways:

this region may be segregated by means of a prism-slit system, or light from a source emitting radiation of high intensity in the 3280 A region can be passed through a suitable filter.

Spekker Spectrophotometer. The most widely used vitamin A measuring instrument of the prism-slit type is the Spekker spectrophotometer. Considerable work has already been done correlating the results obtained with this instrument in different laboratories,[2] as well as comparing its results with those obtained from bio-assays. It is concluded from this investigation that individual laboratories are able to obtain consistent results, and that the results of one laboratory bear a fairly constant relation to those of other laboratories.

Hilger Vitameter. The first instrument for measuring vitamin A using a filter as a monochromator was the Hilger vitameter. In this instrument the filter consists of a thin silver film and a thin plate of Woods glass, the light source being a copper arc. The resulting radiation is shown in Fig. 2 in the spectrum marked Cu-Ag filter. The Hilger vitameter is so well known that little need be said regarding its construction and operation. Extensive comparative tests have been made on it with differ-

ent operators in different laboratories. The results obtained from these tests seem still too varied to warrant its adoption as an official method for vitamin A assay.

Within the last two years three instruments using filters as monochromators, and photoelectric cells as light meters, have been described. Since these instruments make possible very accurate and rapid absorption measurements it seems worth while to describe them in some detail.

Milas-Farmer Photoelectric Photovitameter. The first of these instruments to appear was that of Milas and Farmer.[3]

Fig. 2

In this instrument essentially monochromatic radiation near the 3280 A absorption peak is obtained by passing the radiation from a copper arc through a Corning red ultra No. 597 glass filter. When the transmitted radiation is measured by means of a sodium photocell it is evident from Fig. 3 that the maximum photoelectric currents are obtained from radiation near the 3280 A absorption peak, and that photoelectric currents will be produced over only a relatively narrow range of wavelengths on either side of the 3280 A peak.

In the optical system of this instrument, radiation from a copper arc is separated into two beams, one of which passes through an absorption cell containing a solution of

vitamin A oil, while the other passes through a shutter-controlled aperture. By
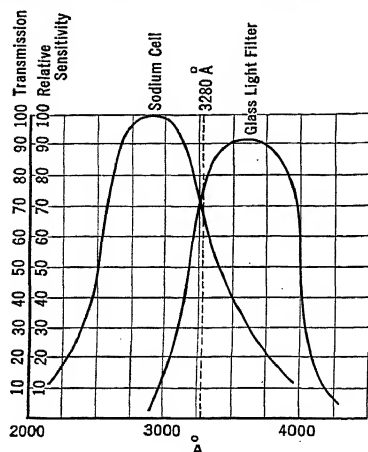

FIG. 3

properly adjusting the area of the shutter-controlled aperture the intensity of the radiation transmitted through it can be made equal to the intensity of the radiation transmitted through the absorption cell. Values of log I_0/I are read directly. Only one photocell is used, and a flicker disk serves to make the separate beams fall alternately on the photocell. In order to eliminate inaccuracies resulting from variations in arc intensity and to produce a suitable frequency the flicker disk is so designed as to produce a 480-cycle current in the photocell.

The photocell currents are amplified by means of a sharply turned amplifier, designed by Professor R. B. Fay, and having its maximum response at a frequency of 480 cycles per second. When the two

TABLE I

COMPARISON OF POTENCIES OF THE U.S.P. REFERENCE COD-LIVER OIL

	E			$E_{1\,cm}^{1\%}$		Vitamin A Potency in U.S.P. Units	
	% Concentration	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
Hilger vitameter	0.4076	0.81	0.68	1.99	1.67	3184	2672
	0.4750*	0.77	....	1.62	....	2592	....
Spectrophotometer	0.5056	0.85	....	1.68	....	2690	....
	0.3618	0.60	....	1.66	....	2660	....
	0.2022	0.35	....	1.73	....	2770	....
				Mean =	....	2710	....
Photoelectric photovitameter	0.5056	0.86	....	1.70	....	2720	....
	0.3618	0.60	....	1.66	....	2660	....
	0.2022	0.37	....	1.83	....	2930	....
				Mean =	....	2770	....
	Biological value					3000	

* Reported by Mr. Francis Tripp, of the E. L. Patch Company.

light beams impinging on the photocell are of equal intensity the frequency of the photocell current is doubled, and the output of the amplifier contains a minimum of the 480-cycle frequency. The instrument is operated by balancing the intensities of the two light beams until a minimum of the 480-cycle output is obtained.

The results obtained by Milas and Farmer with this instrument are shown in Table I. As is evident from the table good agreement is obtained with the spectrophotometer extinction coefficients.

McFarlan-Reddie-Merrill Vitamin A Meter. When radiation from a sodium arc is passed through a Corning Red Purple Corex No. 986 filter the resulting radiation is monochromatic and has a wavelength of 3303 A — only 23 A away from the 3280 A vitamin A absorption peak. The spectrum obtained under these conditions is shown in Fig. 2 in the spectrum marked Na-Corex filter. The sodium arc is glass enclosed, and is consequently free from the variations of open-air metallic arcs. Radiation from the sodium arc is divided into two beams, the intensity of each beam being controlled by a variable-area slit. One of these slits is connected to a logarithmic scale by a mechanism such that $\log I_0/I$ may be read directly. The light beam controlled by this slit passes through an absorption cell containing the diluted oil.

In addition to choosing phototubes with a good response to the 3303 A radiation it is also necessary to use phototubes which do not respond to radiation of wavelengths greater than 7000 A, since the Corex No. 986 filter again begins to transmit radiation above 7000 A. Both sodium and potassium oxide tubes satisfy these requirements. The circuit, designed by F. H. Shepard, Jr., is essentially an alternating-current-operated direct-current amplifier. The method of operating the instrument

is as follows: The absorption cell is inserted in front of the calibrated variable-area slit, which is opened wide. The other variable-area slit is then adjusted to give zero resultant phototube current. Upon the absorption cell being removed and the calibrated variable-area slit being adjusted to give zero resultant phototube current, the value of $\log I_0/I$ can be read directly from the scale attached to the calibrated variable-area slit. With this method of operation any necessity for matched phototubes is eliminated, errors arising from changes in light intensity are automatically eliminated, and the instrument is effectively recalibrated for each vitamin A measurement.

The calibration curve made with the U.S.P. reference cod-liver oil is shown in Fig. 4.
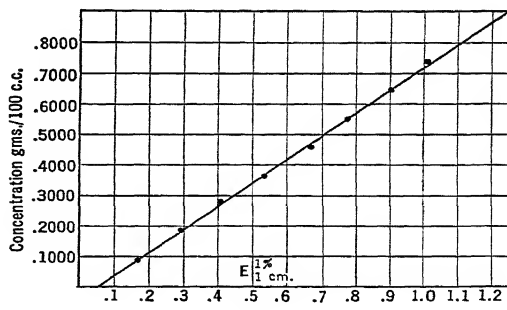

FIG. 4

In this curve each point represents an individual reading, and no correction has been made for the loss of radiation due to reflection from the walls of the absorption cell. Beer's law is seen to hold accurately over a large range of concentrations, a feature which permits considerable flexibility in making dilutions and consequently increases the rapidity with which tests can be made.

In Table II are shown the results of assays made on cod-liver oil samples which

were at the same time bio-assayed. The agreement between the two methods of assay lies well within their respective experimental errors.

TABLE II

Assays of Cod-Liver Oil

Photoelectric Vitamin A Meter — A/Gm	Bio-Assay A/Gm
2650	2576
2740	2576
2480	2100
3200	3900
2710	3170
2760	3900
2440	3900
2500	1930
2100	2180
2100	2100
2200	2100
2150	2675

In Table III are shown the results of assays made on halibut-liver oil samples which were at the same time bio-assayed in two different laboratories. As is to be expected, the variation in the results of the biological assays is large.

TABLE III

Assays of Halibut-Liver Oil

Photoelectric Vitamin A Meter — A/Gm	Bio-Assays — A/Gm	
	Lab. 1	Lab. 2
50,800	50,000	93,000
49,400	50,000	91,000
58,300	50,000	59,090
61,750	50,000	50,000

A comparison of results obtained in oils of various concentrations with those obtained on the same oils with a spectrophotometer is presented in Table IV. The spectrophotometer readings were made at 3280 A, and the photoelectric vitamin A meter readings at 3303 A. The values of $E_{1\,cm}^{1\%}$ — the absorption coefficient of a 1 per cent solution 1 cm thick — are 1.70 and 1.32 for the two wavelengths, 3280 A and 3303 A, respectively. The close agreement between the two sets of results indicates that Beer's law holds for monochromatic radiation at either wavelength, and that the two extinction coefficients bear a constant relation to each other that is independent of the concentration of the vitamin A solution.

TABLE IV

Photoelectric Vitamin A Meter — A/Gm	Spectrophotometer — A/Gm
25,590	25,450
32,230	32,100
78,890	74,040
102,200	98,010
177,800	176,760

Bills-Wallenmeyer Electronic Photometer.[5] When radiation from an argon glow lamp is filtered through red-purple Corex glass and nickel chloride solution the spectrum of the resulting radiation shows two lines, both of which come within the absorption limits of the vitamin. The two lines fall on either side of the absorption maximum, as is seen in Fig. 5. In this figure are shown a plain hydrogen discharge tube spectrum, the absorption spectrum of vitamin A superposed on the hydrogen spectrum, unfiltered argon glow lamp radiation, filtered argon glow lamp radiation, and a composite of filtered argon glow lamp radiation plus the absorption spectrum of vitamin A.

The lower power consumption of the argon glow lamp, combined with an unusually stable amplifier, has resulted in a compact, portable instrument that yields reliable vitamin A measurements. Results are obtained by referring all readings to a
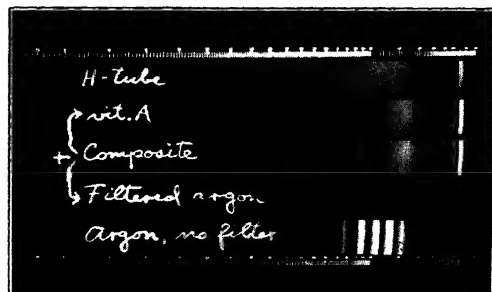

FIG. 5

calibration curve made with the U.S.P. reference cod-liver oil. In its present form the instrument is not designed to measure extinction coefficients.

Still another type of spectrophotometric

method for the assay of vitamin A has recently been developed.[6] This method depends on the rate of destruction of vitamin A when irradiated with ultraviolet light. The total absorption of the solution of vitamin A is determined, and then the solution is irradiated with filtered light of 3650 A until the absorption peak at 3250 A disappears. Vitamin A is destroyed, and a new substance having two-thirds of the total absorptive power of vitamin A is formed. The total absorption of the solution is again determined, and the difference, multiplied by 3, gives the vitamin A content of the original solution.

In the preceding discussion of the application of spectrographic methods to the determination of vitamin A it has been tacitly assumed that the vitamin A absorption curve is independent of the source from which the oil is obtained. Evidence has recently been advanced, however, which indicates that this assumption is not always correct. In Table V are listed

TABLE V

ULTRAVIOLET ABSORPTION OF LIVER OILS AND CONCENTRATES

Marine Fish			Fresh-Water Fish		
Type of Fish and Nature of Sample	Maximum m μ	$E_{1\,cm}^{1\%}$	Type of Fish and Nature of Sample	Maximum m μ	$E_{1\,cm}^{1\%}$
Halibut (oil)	328	71.5	Pike (oil)	345 280	6.0 5.2
Halibut (unsaponified)	328	113.0	Pike (concentrated)	344 280	8.5 7.5
Dogfish (oil)	325	1.7	Salmon (oil)	349 282	14.2 11.8
Haddock (oil)	327	2.56	Salmon (concentrated)	340 280	17.8 18.4

some absorption maxima and the corresponding values of $E_{1\,cm}^{1\%}$ for both marine liver oil concentrates and fresh-water fish-liver oil concentrates.

Feeding tests so far made indicate that there is no significant difference in the biological activity of the two types of fish-liver oil concentrates, a fact which has given rise to speculation regarding the possible existence of a second vitamin A, known as vitamin A_2. Consequently, when spectrographically determined absorption coefficients are translated into units of biological activity, the source of the fish-liver oil must be taken into account. However, since the major sources of vitamin-A-containing oils are, at present, either cod-liver oil or halibut-liver oil, both of which have their absorption peak at 3280 A, the possible existence of vitamin A_2 is not yet of great importance commercially.

In conclusion it may be said that when proper precautions are observed spectrographic methods of vitamin A assay afford very rapid, accurate, and reliable results.

REFERENCES

1. MORTON, "The Absorption Spectra of Vitamins and Hormones," p. 21.
2. "Report of A.D.M.A. Vitamin Assay Committee," *J. Am. Pharm. Assoc.*, 26, 525, 1938.
3. N. A. MILAS and R. H. FARMER, presented at Pittsburgh Meeting, Am. Chem. Soc., September, 1936.
4. McFARLAN, REDDIE and MERRILL, *J. Ind. Eng. Chem.*, 9, 324 (1937).
5. BILLS and WALLENMEYER, presented at Baltimore Meeting, Am. Soc. Biol. Chem., April, 1938.
6. DE, *Indian J. Med. Research*, 23, 505, 1935. CHEVALLIER and DUBOULLOZ, *Bull. soc. chim. biol.*, 18, 190 (1936).
7. GILLAM, HEILBRON, JONES, and LEDERER, *Biochem. J.*, 32, 405 (1938).

APPLICATIONS OF ULTRAVIOLET ABSORPTION SPECTRA IN ESTABLISHING THE STRUCTURE OF VITAMIN B₁

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The determination of the structure of vitamin B_1 was the achievement of a group of workers under the leadership of Dr. R. R. Williams. The interpretation of the absorption curves in their relation to the chemical structures involved was likewise not an individual accomplishment. Ideas were contributed by various members of the group and particularly by Dr. Williams. The experimental methods and the data have been published in the *Journal of the American Chemical Society* and were there discussed from the viewpoint of the structure of the vitamin. It seemed, however, that a review which stresses the role of absorption spectra in this type of work might be of interest.

The vitamin was first isolated in pure form by Jansen and Donath in 1926, but it was not until several years later that sufficient material became available for chemical study. In 1933, Williams and his co-workers obtained sufficiently large yields[1] to undertake the study of the chemical structure. This study was begun using a reaction which quantitatively (97 per cent) split the vitamin into two portions:

$$C_{12}H_{17}N_4OSCl + H_2SO_3 \longrightarrow$$
$$\underset{\text{I}}{C_6H_9NOS} + \underset{\text{II}}{C_6H_9N_3SO_3} + HCl$$
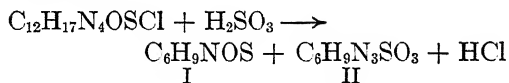
Considering I first, several important reactions were found. The first of these was the reaction with hydrochloric acid to give the product C_6H_8NSCl. The spectra of these two compounds are nearly identical,[2] and this result indicates that the hydroxyl group substituted by chlorine is on a side chain. Upon addition of methyl iodide a quaternary salt was formed, and upon oxidation with nitric acid the following reaction occurred:

$$\underset{\text{I}}{(C_4H_4NS)}-C_2H_4OH + \overset{(HNO_3)}{\longrightarrow} \underset{\text{III}}{(C_4H_4NS)COOH}$$
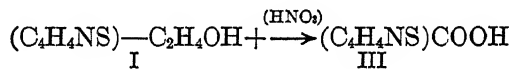
Windaus in Germany had prepared what proved to be III by direct action of nitric acid on the vitamin, and Smakula,[3] working in Windaus' laboratory, had noted a similarity of absorption between this compound and derivatives of pyrrole. This similarity, as we shall see, proved to be fortuitous. Judging by the reactions already given, the compound could be either a pyrrole or a heterocyclic compound in which sulfur is included in the ring structure. Thiazole is such a compound, and several thiazoles were prepared for comparison with cleavage product I. The close similarity is evident in Fig. 1.[2] Now, on formation of the quaternary salt with methyl iodide, a marked shift and increase in intensity of the absorption band was to be noted. With 4 methyl thiazole the same shift and increase in intensity was also evident, as

shown in Fig. 2.[2] Such a similarity in two derivatives greatly increases the probability of identity of the fundamental ring structure. On synthesis of III the virtual identity of spectra of the synthetic and natural products was evident.[2] It should be pointed out that the strong evidence for the presence of the thiazole ring in the cleavage product many weeks prior to
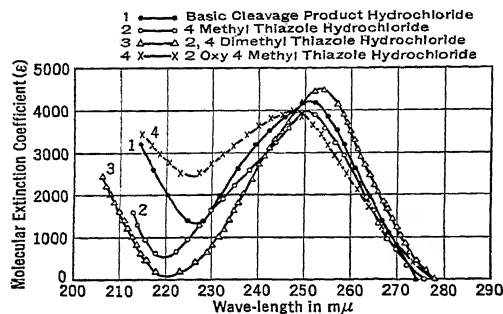

1 ●——● Basic Cleavage Product Hydrochloride
2 ○——○ 4 Methyl Thiazole Hydrochloride
3 △——△ 2, 4 Dimethyl Thiazole Hydrochloride
4 ✕——✕ 2 Oxy 4 Methyl Thiazole Hydrochloride

FIG. 1

the final identification of the compound permitted us to neglect other possibilities, and to go ahead with certainty that we were on the right track. Eventually, product I was synthesized and proved to have the following structure:

$$\begin{array}{c} CH_3 \\ | \\ C = C - CH_2CH_2OH \\ \end{array}$$
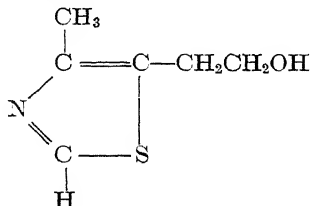
Titration of this compound and its derivatives by means of the glass electrode proved that the thiazole exists in the vitamin in the form of a quaternary derivative. Thus, the structure and linkage through nitrogen of this product to the rest of the vitamin were thoroughly established. Obviously, not only from its method of

formation but also from its properties, the other cleavage product (II) was a sulfonic acid. Attempts to split off the SO_3H group by hydrolysis were unsuccessful. However, in the presence of hydrochloric acid, an important reaction occurred:

$$C_6H_9N_3SO_3 + HOH \xrightarrow{\text{(HCl)}} C_6H_8N_2SO_4 + NH_3$$
$$\quad\text{II} \qquad\qquad\qquad\qquad\quad \text{IV}$$
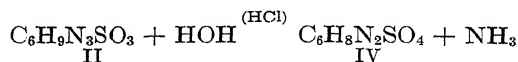
In product IV formed by this reaction an OH group replaced the NH_2 group originally present. A pyrimidine nucleus in

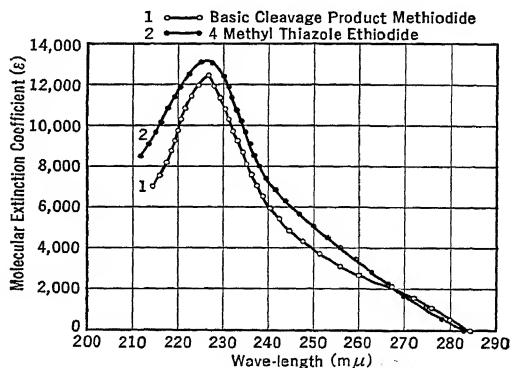1 ○——○ Basic Cleavage Product Methiodide
2 ●——● 4 Methyl Thiazole Ethiodide

FIG. 2

vitamin B_1 had been suggested by numerous workers, and the above reaction is consistent with 2 amino and 6 amino pyrimidines. In Fig. 3[4] the absorption spectra of II is compared with 2 amino and 6 amino pyrimidines. Note the similarity with the 6 amino and the contrast with the 2 amino. The same principle used in connection with the other portion of the molecule was again employed here, and in Fig. 4[4] a comparison is seen between the oxy derivative (IV) of the cleavage product and the 2 oxy and 6 oxy derivatives. Note the shift in the absorption bands and the similar shift with 6 amino pyrimidine and the marked contrast in both cases with 2-substituted

pyrimidines. In this connection it is interesting to note also a shift in one of the absorption bands of the vitamin when an amino group is replaced by OH.[5] We thus had proof of the presence of a pyrimi-

1. Amino Sulfonic Acid.
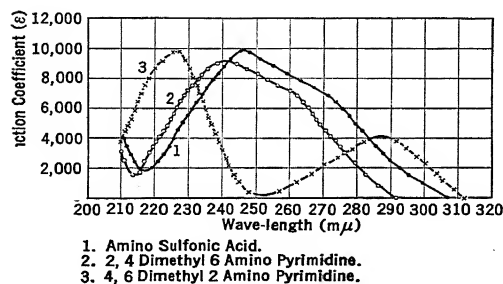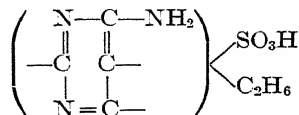2. 2, 4 Dimethyl 6 Amino Pyrimidine.
3. 4, 6 Dimethyl 2 Amino Pyrimidine.

Fig. 3

dine ring and strong evidence for the location of one of the substituent groups months before the complete structure of this cleavage product was known, and again could go ahead with confidence that other configurations were excluded.

In connection with the work on pyrimidines another kind of service was frequently performed by absorption methods. Pyrimidines are commonly prepared by condensing two chain compounds, and this involves coupling at two places. When preparing a new compound, if conditions were too mild it sometimes happened that coupling occurred at only one point but complete ring closure had not taken place. Such a compound would not exhibit any marked selective absorption. It was thus possible without making quantitative measurements or even completely purifying the product of a reaction to tell the organic chemist whether or not he had formed a pyrimidine and thereby save him hours of precious time.

To get back to our molecule, we now had fairly good evidence as to the structure of most of this portion except for

C_2H_6 with three places in which to partition these atoms. There are six possible isomers for different allocations of the

$$\left(\begin{array}{c} N-C-NH_2 \\ \| \quad \| \\ -C \quad C- \\ \| \quad \| \\ N=C- \end{array}\right)\!\!\!<\begin{array}{l}SO_3H\\ \\C_2H_6\end{array}$$

C_2H_6 and three places for each isomer in which to put the SO_3H which tags the original location of the other ring. At

1. Oxy Sulfonic Acid.
2. 2, 4 Dimethyl 6 Oxy Pyrimidine.
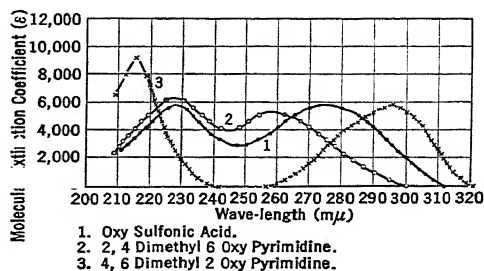3. 4, 6 Dimethyl 2 Oxy Pyrimidine.

Fig. 4

this point a new cleavage of the vitamin was discovered. In liquid ammonia the vitamin is split into $C_6H_{10}N_4$ (V) and a number of smaller fragments. This new product turned out by elementary analysis to be a diamino compound. The three possible diamino isomers were prepared with one NH_2 in the 6 position. In Fig. 5[6] are shown the absorption spectra of V and the spectra of these isomers. The contrast in absorption is marked in each case. However, the absorption of the cleavage product is quite similar to the absorption of alkylated 6 amino pyrimidines even when other groups are substituted on a side chain. This was the first evidence of a methylene bridge between the two nuclei of the vitamin and cut down the possible isomers from eighteen to nine.

By reaction of the original cleavage product II with sodium in liquid ammonia, the

sulfite group was finally split out and the resulting compound turned out to be identical with 2,5-dimethyl-6-amino pyrimidine. Thus, we had identified the other portion of the vitamin furnished by the sulfite cleavage. We still had, however, the problem of which methyl is attached to the thiazole. Consideration of the evidence as to the structure of thiochrome, an oxidation product of the vitamin, led us to prefer the 5 position. This was confirmed
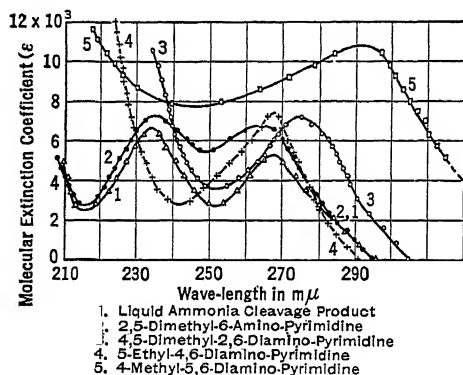

Fig. 5

by synthesis of the oxysulfonic acid (IV) from 2-methyl-6-oxy-5-ethoxymethyl pyrimidine, thus proving that the attachment is through the methyl group in position 5.

In connection with the identification of this oxysulfonic acid, an interesting application of absorption spectra was utilized. Although there was close agreement in absorption[6] between the natural and the synthetic products, we did not regard this evidence as sufficient proof of identity, and, since the compound does not melt, the

conventional method of mixed melting points was not possible. As a comparable test, a mixed solubility absorption test was devised. It consisted of comparing the absorption at all wavelengths of a saturated solution in absolute alcohol of (*a*) the synthetic, (*b*) the natural, and (*c*) an equal mixture of the two. If the substances were not identical (*c*) would have approximately twice the absorption of either (*a*) or (*b*) and there would be no match throughout the region of absorption. However, since an excellent match throughout was obtained, this was taken as a positive test of identity. Thus was the final detail of the structure of the vitamin fixed, and within a very short time the vitamin was synthesized and found to be identical in all respects with the natural product.[7]

Vitamin B₁ (hydrochloride)
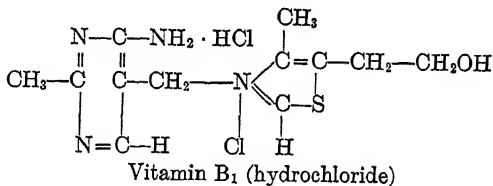
REFERENCES

1. WILLIAMS, WATERMAN, and KERESZTESY, *J. Am. Chem. Soc.*, 56, 1187 (1934).
2. RUEHLE, *ibid.*, 57, 1887 (1935).
3. SMAKULA, *Z. physiol. Chem.*, 230, 231 (1934).
4. WILLIAMS, BUCHMAN, and RUEHLE, *J. Am. Chem. Soc.*, 57, 1093 (1935).
5. BUCHMAN and WILLIAMS, *ibid*, 57, 1751 (1935).
6. CLINE, WILLIAMS, RUEHLE, and WATERMAN, *ibid*, 59, 530 (1937).
7. CLINE, WILLIAMS, and FINKELSTEIN, *ibid.*, 59, 1052 (1937).

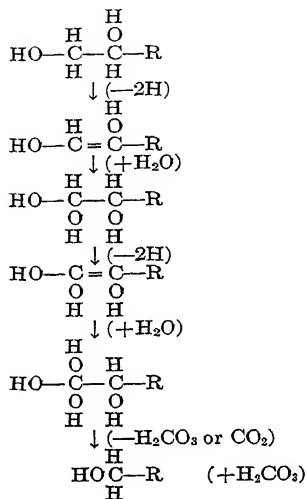# SPECTROSCOPIC STUDIES ON ENZYME SYSTEMS

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University of Chicago

The present report deals with the application of absorption spectroscopy to the study of enzyme reactions and has the purpose of projecting the role of this branch of the physical sciences into the future study of this very important subject. When I speak of enzyme reactions, I refer to the respiratory enzymes, for, as yet, I know of no application of spectroscopy to proteolytic or hydrolytic enzyme systems. It is only those systems which involve oxidation and reduction to which spectroscopy may be applied. Let me first demonstrate the reason for this.

In much of the work that has been carried out in this field, no serious attempt has been made to isolate the enzyme or enzymes responsible for the oxidation of a particular substrate, nor up to very recently have many serious attempts been made to isolate the various steps involved in the complete oxidation of the particular substance in question. Only the over-all reaction, for the most part, has been considered. One knew that oxygen and substrate are consumed, and that water and carbon dioxide were evolved. It was natural to assume that through some form of activation (by the enzyme) the oxygen

and substrate were rendered capable of combining with each other — oxygen molecules (or atoms) combining with carbon atoms of the substrate to form carbon dioxide, and with hydrogen atoms of the substrate to form water. It was not until the Wieland Thunberg mechanism of oxidation was expounded that a clearer insight into these processes was obtained. According to this hypothesis, which has been substantiated by experiment, oxygen does not combine directly with carbon atoms, but the process of oxidation of the substrate, for the majority of cases, consists in the removal of hydrogen atoms, i.e., dehydrogenation. In many cases, oxidizing agents are hydrogen acceptors, and reducing agents, hydrogen donators. When a reducing agent is oxidized, it loses two hydrogen atoms, and, usually, this results in the formation of a double bond. Oxidation-reduction is then the formation and disappearance of double bonds. Carbon dioxide is formed by successive processes involving the removal of two hydrogen atoms and the replacement of these two atoms by a water molecule (an H and an OH radical) with the consequent splitting of CO_2 (or H_2CO_3) from the molecule.

31

This I can illustrate schematically as follows:

$$
\begin{array}{c}
H \\
HO \\
HO-C-C-R \\
HH \\
\downarrow (-2H) \\
H \\
HO \\
HO-C=C-R \\
\downarrow (+H_2O) \\
HH \\
HO-C-C-R \\
OO \\
HH \\
\downarrow (-2H) \\
HO-C=C-R \\
OO \\
HH \\
\downarrow (+H_2O) \\
H \\
OH \\
HO-C-C-R \\
OO \\
HH \\
\downarrow (-H_2CO_3 \text{ or } CO_2) \\
H \\
HOC-R \quad (+H_2CO_3) \\
H
\end{array}
$$

With the formation or disappearance of double bonds, the absorption spectrum of the donator or acceptor of hydrogen changes, and it is this change in absorp-
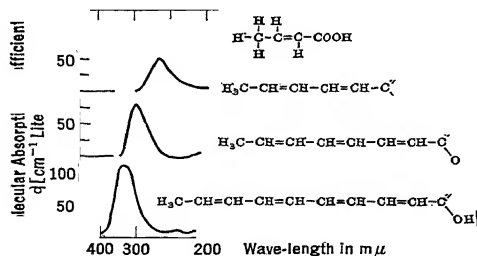
FIG. 1.   Change in Absorption Spectra with Change in Number of Conjugated Double Bonds.

tion spectrum which affords a means of following the course of enzyme reactions.

Hausser, Kuhn, and their co-workers have made an extensive study of the relationship between the number of conjugated double bonds, and the position and absorption coefficient of the peak of the absorp-

tion spectrum. Both the position of the absorption maximum and the absorption coefficient of the maximum vary in a
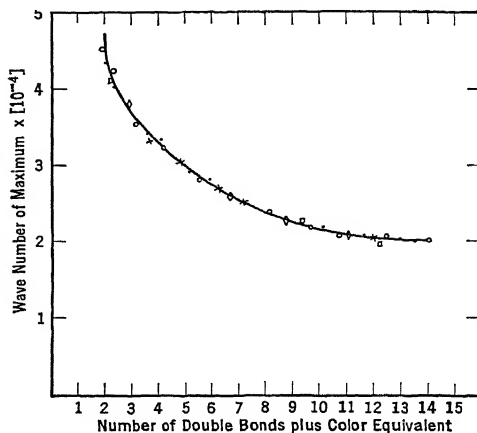

FIG. 2.   Portion of Maximum of Absorption Band for 65 Different Substances as a Function of the Number of Conjugated Double Bonds.

regular manner, as shown in Figs. 1 and 2. These graphs have been constructed from their work.   In Fig. 1 it will be observed that the absorption coefficient varies linearly with the number of conjugated bonds, while the position of the maximum shifts toward the red as the number of bonds is increased.   The results of the study of 65 dyestuffs are shown in Fig. 2.   Here, the position of the maximum is plotted against the number of double bonds.   In every case, a correction is made for the color equivalent of some end group.   For example, a carboxyl group, when combined in a conjugated way with a double bond, has an equivalent shift of one carbon to carbon double bond, while a benzene ring contributes one and one-half conjugated bonds.   From these results it becomes apparent that, when a compound is hydrogenated (i.e., when the number of conjugated bonds is changed), there results a

marked change in the position of maximum absorption.

The function of some of the respiratory enzymes is that of taking away two hydrogen atoms from the substrate molecule, and passing them on to some hydrogen acceptor. For those cases which have been investigated thoroughly, it has been found that the enzyme itself consists of a prosthetic group known as the co-enzyme, or partner, which is combined with a protein, which, for want of a better name, is known as the enzyme proper. The prosthetic group is the active group which, in some cases, has been identified with one of the vitamins and contains conjugated double bonds, one of which is capable of accepting two hydrogen atoms and, in turn, passing them on to some other acceptor. Fig. 3 illustrates this process for diphospho-
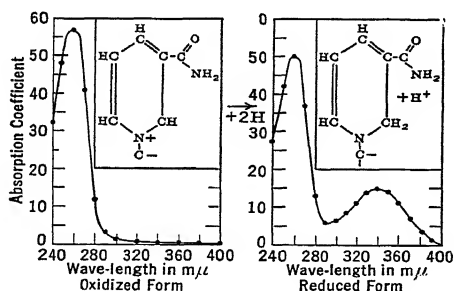
Fig. 3

pyridin nucleotid. The co-enzyme shown here is not complete and is designated only by the essential nucleus which does the hydrogen accepting. The absorption spectra and formulas of the normal and hydrogenated forms are shown. This nucleus is the amid of nicotinic acid and is the pellagra-preventing vitamin. Adenylic acid and two phosphate groups, together with a protein partner, are attached to this molecule when it is in its active catalytic form, in which form it

has the capacity of oxidizing alcohol. When two hydrogen atoms are added to the group, a new band is formed with a maximum at 3400 A. By using this peak for analytical purposes, Negelein and Wulff, after isolating and purifying this enzyme, have studied the kinetics of the reaction between it and its substrate alcohol, and have obtained rather complete information about the first step of the oxidation. A very similar enzyme triphosphopyridin nucleotid is responsible for the oxidation of hexose monophosphate (i.e., sugar rendered active by other enzymes), and this enzyme too has been similarly studied, but not so exhaustively.

After this first step in the oxidation (or dehydrogenation) of sugar, there are two distinctly different paths of research which may be followed: one is to trace the fate of the oxidized sugar molecule, and the other is to follow the two hydrogen atoms, which, at this point in the development of our subject, are attached to the prosthetic group of the triphosphopyridin nucleotid. The first-mentioned approach, following the sugar molecule, is that of a great number of research workers in this field and, particularly, of the school headed by Meyerhof. Warburg, Theorell, Szenti-Gyorgi, and Keilin are among the principal workers in the field which traces the course of the two hydrogen atoms.

Oxygen will not act directly with the hydrogenated form of the diphosphopyridin nucleotid, and, before these hydrogen atoms form water, they must be passed on to at least one more acceptor. Theorell has demonstrated that the oxidized form of Warburg's yellow ferment, the formula and absorption spectrum of which are shown in Fig. 4, has this capacity. This compound reacts with the reduced prosthetic group of the di- or triphosphopyridin nucleotid and accepts the two hydrogen

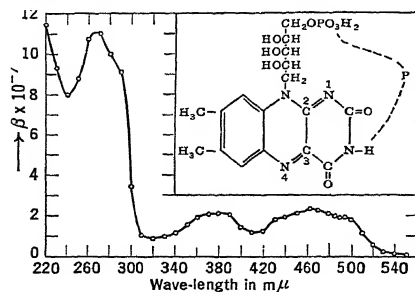atoms in question. These now attach themselves to the nitrogen atoms numbered

FIG. 4

1 and 4, and a double bond forms between carbon atoms 2 and 3, thus destroying the conjugation and changing its absorption spectrum in such a way that there is practically no absorption in the region of the two bands of the oxidized form. The velocity of this reaction, too, has been studied using the absorption spectrum as the analytical tool.

The hydrogenated form of this compound will react directly with oxygen; it is also oxidized by cytochrome-C, which, in turn, through other enzymes, can be re-oxidized by oxygen. The possible paths by which the two hydrogen atoms may be converted to water are given in Fig. 5, for the reproduction of which I am indebted to my colleague, Dr. Elmer Stotz. It will be
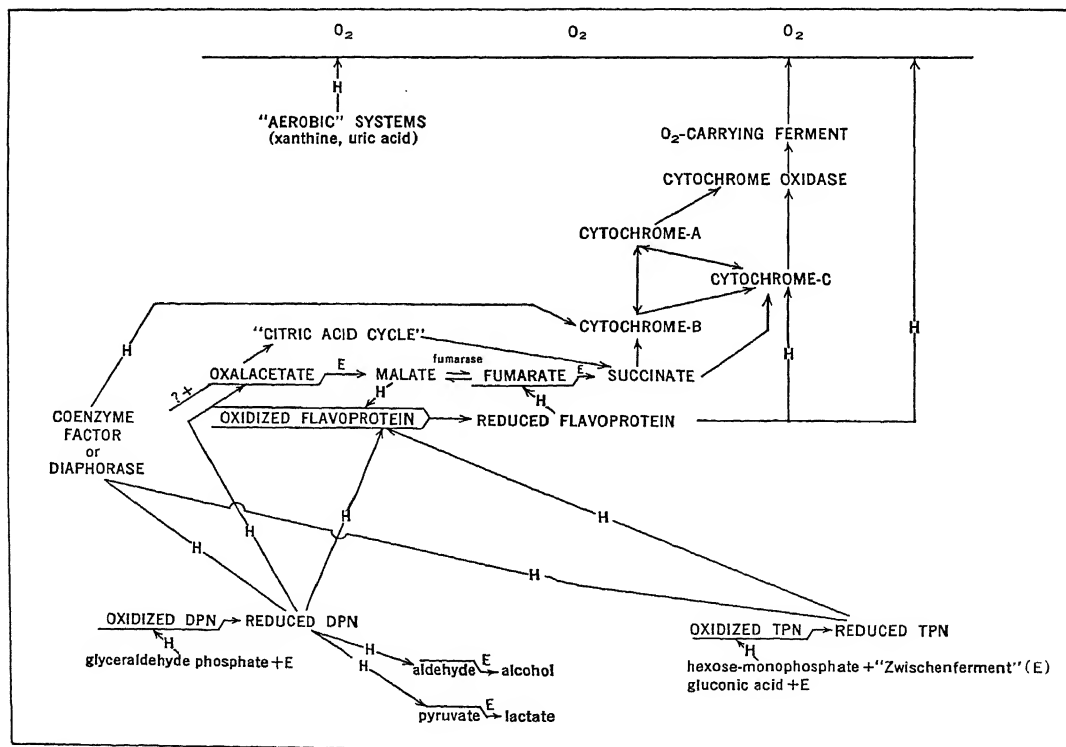
FIG. 5

observed that the two enzymes we have discussed appear at the lower part of the figure. Oxygen is at the tip, and, before the oxygen and the wandering hydrogen atoms are completely converted to water, they must traverse at least one of the paths indicated in this diagram. These paths have been demonstrated or rendered probable by qualitative and rather gross experiments, the details of which have not been investigated. The "indophenol oxidase," or cytochrome oxidase, is known to exist, but its exact nature and function will be known only as the result of future experiment. Each of these steps involves an enzyme oxidation reduction reaction, and all the substances involved should show changes in their absorption spectra when undergoing either oxidation or reduction. In each case the detailed study of these reactions can be made with the spectrograph.

From a physicochemical point of view, these reactions can best be understood by the obtaining of two sets of data. One involves the free energy changes occurring in each of the reactions. From such information, some reactions may be ruled out, and others included as possibilities. The other is a study of the kinetics of each reaction under all conditions of concentration, pH, and temperature. With this information we may then be able to determine the normal course of oxidation and understand the abnormal case such as that involved in diabetes.

I have given examples of the spectroscope attack on the study of the reaction velocities. An example of equilibrium study, i.e., free energy change, I choose from our own laboratory. Free energy changes for any reaction may be calculated if the electric potentials of each oxidizing-reducing couple involved in a complete enzyme reaction are known. These data

(potentials) can often be obtained electrometrically, but sometimes this is impossible because of the slowness of reaction between the substances in question and the electrodes. Then, too, the electrometric method necessitates relatively large amounts of material, and only the smallest amounts of enzymes are ever available because of their low concentrations in the living cell. A spectrometric method has been developed at Chicago which requires only the smallest amounts of material and does not depend upon the reactivity of the substance with any electrode. This method consists in bringing the enzyme into an oxidation-reduction equilibrium with some substance (usually a colored dyestuff) for which the potential is known, and if the potential of the reference substance is known, the potential of the enzyme can be calculated from a knowledge of the concentrations of all the substances present under equilibrium conditions. These equilibrium concentrations can be determined spectrographically. In this way, we have determined the potential of cytochrome-C, one of the very important respiratory enzymes. In Fig. 6 are shown the absorption spectra of the oxidized and reduced forms of both the enzyme and one of the reference dyestuffs. Cytochrome-C, unlike the other enzymes to which I have referred, contains an iron atom which is oxidized from the ferrous to the ferric state. Unlike the other enzymes, it is not a hydrogen carrier. After the oxidized enzyme and the reduced dye are brought together, some of the enzyme is reduced and some of the dyestuff oxidized. By the proper selection of wavelengths the concentrations of all substances involved may be determined. It is apparent how the analysis can be made by the determination of the amount of light absorbed at selected wavelengths. By using several different

reference substances, the potential of cytochrome-C was determined to be $+0.262$ volt, a value which is quite independent of pH. These data are illustrated in Fig. 7. With this knowledge we can now predict some of the possible substances with
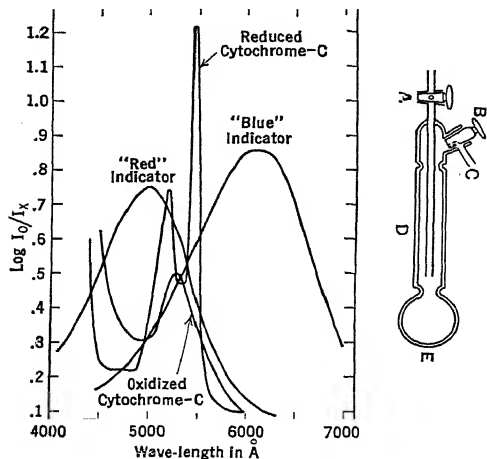

FIG. 6

which cytochrome-C can react and more particularly with what substances it cannot react with any appreciable velocity.

• It has been my purpose to show that, in spite of the complexity of the respiratory enzyme problem, substantial progress is being made in an understanding of it. The spectrograph has been a very deciding factor operating to this end. With the older and usual enzyme technique, only the total effect of all cellular processes involved can be studied, but with the spectrograph each individual step can be isolated.

The path that has been opened in this field leads us to ask some interesting questions:

1. Every enzyme has associated with it some large protein partner. What is the function of the protein? Is it that of re-

ducing the activation energy of the prosthetic group? Is it a source of energy (each degree of freedom not "frozen" may contribute $\frac{1}{2} RT$ calories, and a protein molecule must have many such degrees of freedom)? Does it exert a steric influence on the reacting molecules, i.e., align them in an optimum position for reaction? Or does its large surface offer a means by which molecules "crawling" over it, as a two-dimensional gas, can come into rapid contact with each other? Only a detailed knowledge of the kinetics of these reactions will give an insight into these questions.
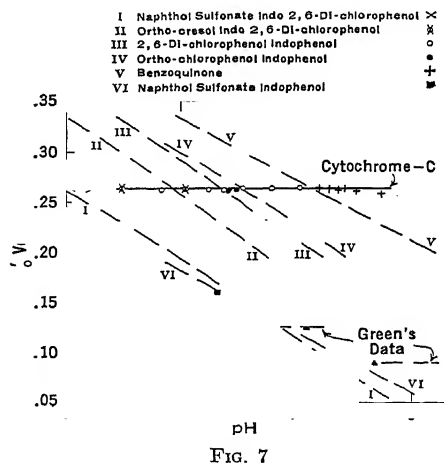

FIG. 7

2. Some intermediate enzymes, such as yellow ferment, undergo a valence change of two when oxidized or reduced; some substances, such as cytochrome-C, undergo a valence change of one. What is the result then when a molecule like cytochrome-C reacts with one like yellow ferment? Is a free radical the result of the first step in the reaction? Again, kinetic studies may give the answer.

3. Why is it necessary for the hydrogen atoms (removed from sugar) to pass

through so many "hands" before it is changed to water? Is this process more nearly a reversible one, and will it, therefore, produce a greater amount of muscular work?

The spectrograph may play no small part in answering these questions.

Lastly, I should like to mention the relationship between respiration and growth. These two processes go hand in hand. Is abnormal cell growth associated with abnormal respiration? Very probably this is the case, and an understanding of the problem of cancer may lie in a better understanding of cellular respiration. I make the prediction that the spectrograph will play a large role in our final understanding of this disease.

REFERENCES

1. K. U. HAUSSER, *Z. tech. Physik,* **15,** 10 (1934).
2. NEGELEIN and WULFF, *Biochem. Z.,* **293,** 351 (1937).
3. O. WARBURG, *Ergeb. Enzymforsch.* VII, p. 210 (1938).
4. H. THEORELL, *ibid.,* VI, p. 111 (1937).
5. D. KEILIN, *ibid,* II, p. 239 (1933).
6. HOGNESS, ZSCHEILE, and SIDWELL, *J. Phys. Chem.,* **41,** 379 (1937).
7. STOTZ, SIDWELL, and HOGNESS, *J. Biol. Chem.,* **124,** 11 (1938).

ON IDENTIFYING MINERALS WITH THE AID OF THE SPECTROGRAPH

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Introduction. Although the title of this paper refers specifically to minerals, it should be obvious that an approach or technique so designed should be applicable not only to ores and rocks but also to synthetic materials and mineral products such as slags, refractories, ashes, residues, ceramics, and pigments. It appears also that excitation by means of the arc, whether of the interrupted type or not, seems more satisfactory as a whole, particularly where a homogeneous character is lacking, or in dealing with the so-called non-metallic minerals or those of a refractory nature.

It is not our purpose to go into details of spectrographic manipulative technique, but it may be mentioned that sample weights conventionally chosen at 50 mg may range from 5 to 200 mg, and that electrodes, conventionally of a suitable grade of graphitized carbon, may well vary in diameter from 1/16 to 5/16 inch. At times on very special work a metallic electrode such as the very high-purity copper at last available might offer advantages. In our practice the lower or sample electrode has been made positive. Ordinarily from 5 to 12 amperes from 220-volt d-c lines are employed with the sample burned to completion, using a sector of suitable adjustment so that a 30- to 45-second sampling of the light emitted will give a plate of suitable over-all density. In general, position 4 or 5 on the large Bausch and Lomb Littrow-type quartz spectrograph, covering the range 2500 – 3600 A, will serve for the elements in question.

Needless to say, in view of the small amount of material employed and the great sensitivity of the method when applied to ores, slags, etc., every precaution should be taken to make sure that the sample is representative and uniform in composition. In determinative mineralogy the use of a stereobinocular microscope is convenient. This may be supplemented by a petrographic examination. A small crystal, fresh cleavage, or other selected fragment is always very desirable. One may arc the fragment or powder therefrom directly, though at times on certain refractory materials this should be supplemented by arcing the powdered mineral mixed with an equivalent weight of powdered carbon.

This practice is in fact recommended for all unknowns suspected to be of a non-metallic or refractory nature. Incidentally the carbon removed in drilling craters or holes in graphitized electrodes will suffice.

It is rather strange to consider that, although perhaps some twenty-seven hundred minerals are recognized, composed of some eighty-seven elements, only one comprehensive attempt appears to have been made

to correlate them and that in a little-known monograph published by Putnam in 1925 and entitled " A Chart Showing the Chemical Relationships in the Mineral Kingdom." This unique treatise lists 1590 minerals, tabulating them according to their composition. It has therefore been made the basis of this paper, which was indeed foreshadowed by Putnam[1] in August 1924, in " Notice of a Determinative Scheme " (p. 12 of " A Chart Showing the Chemical Relationships in the Mineral Kingdom "), from which we quote: " It is obvious that a *determinative scheme* embracing the mineral kingdom, and developed on the plan of successively testing for specific elements, *by blowpipe and wet chemical methods,* would be the logical complement to this chart. Such a scheme was indeed developed during the winter and spring of 1920 . . . by Dr. Warren at the Massachusetts Institute of Technology." This was expanded in 1925 so as to include all minerals.

Our contribution to the foregoing consists mainly in suggesting and tentatively exploring the possibilities in applying the spectrograph to the identification of the constituent elements in minerals, the recasting of Putnam's chart in a more convenient form, with the introduction of such supplementary determinative data as seems advisable, together with some observations on the interpretation of results attained, with the hope that a scheme may be worked out through which the majority of common minerals and many of the rarer ones may be identified with a fair assurance of certainty. It is a little surprising that Putnam makes mention of using the spectrograph for the qualitative determination of the elements merely by inference, particularly in view of the long list of them whose existence was first disclosed with this instrument, although it is true that the technical world has become more spectrographically conscious in the meantime.

PUTNAM'S DEFINITION OF A MINERAL

As it is very helpful to know just what is meant by a mineral, and Putnam's definition can scarcely be improved; it is herewith presented *in toto*:

"A mineral is here understood to be an aggregate of atoms whose physical state is the solid, whose crystallographic and optical constants vary within specific limits, whose chemical composition varies within specific limits, and which has been formed in nature under cosmic, atmospheric or telluric conditions or electrochemical equilibrium." A few exceptions are noted: Hg, He, A, and a group of colloid gels.

THE MECHANICS OF PUTNAM'S CHART

Putnam's chart consists of ninety vertical columns and fifty-four horizontal ones. Each horizontal column represents an element which occurs in nature either as the *dominant electropositive* constituent of a mineral (Ba in barite, $BaSO_4$), or uncombined, but in mineral form (Bi, native bismuth).

The vertical columns indicate all the elements (including ammonium) occurring naturally in the *electropositive* state, as minor constituents; those elements found as *electronegative* constituents, *dominant or subordinate;* the common electronegative radicals; the water molecule; three then unknown elements (Ma, Il, and Re); and the native elements.

Thus, the *dominant electropositive* elements are plotted against all the electropositive elements and all the *electronegative* ones, and against the common radicals, forming 4860 boxes of which only 1021 (21 per cent) are occupied.

Each mineral has been given an arbitrary number, indexed and entered in the chart according to composition, and may appear in several boxes.

Complex species with more than one electropositive element are weighed by their respective percentages and assigned in accordance.

Certain oxygenated radicals for which no coordinate provision is made are entered in the oxygen box of the appropriate horizontal column.

Some radicals, too, are written with x and y subscripts, indicating more than one acid.

The rare earths are grouped under the type elements Ce and Yt, this classification being a practical approximation.

ADVENTITIOUS VICARIOUS ELEMENTS

As a rule, the presence of certain minor constituent elements, including both common and rare ones, has been assumed adventitious and disregarded except in the case of very pure material, consistent occurrence from different localities, and isomorphous replacement by an associate. These elements are especially prevalent in non-metallics and may occur from a trace to several per cent.

The spectrograph shows that Ga and Ge, and In in particular, for instance, not only are widely diffused in small quantities, but also display a marked tendency to concentrate themselves in certain hosts, for which they are therefore entered as a minor constituent.

It is not always easy, however, to distinguish between minor elements which are actually a part of the mineral, and those which are absorbed, occluded, or mechanically mixed, and, in such cases, increasing reliance must be placed on supplementary tests, especially the specific gravity.[2, 3]

PURITY OF MINERALS

Some may be under misapprehension as to the purity of minerals, regarding them as merely approximately pure. This would be an error. It should not be forgotten that geology has an endless supply of one requisite for synthesizing minerals of which man has next to nothing — unlimited time! With its aid, nature can perform some simple miracles which still defy the best efforts of the chemist, such as the synthesis of *calcite* (calcium carbonate). So far as we know, the best calcium carbonate which is commercially available or which has been made is quite impure from even the chemical standpoint since it is a product of double decomposition and necessarily absorbs any and all concomittant impurities present in the solution. Tacit recognition of this fact is made by the analytical chemist in his use of Iceland spar as a reagent for the standardization of acid solutions. However, he should be on his guard with even the clearest of spar against the presence of considerable of the ubiquitous and isomorphous *dolomite* (magnesium carbonate). Nevertheless, high-purity native calcium carbonate is not uncommon, and one of us sought and found such a spar some years ago from Big Timber, Sweet Grass County, Montana, when it was desired to have pure calcium chloride as a tracer or internal standard.

Water precipitated in the form of clouds in the highest strata of the atmosphere should be spectrographically pure inasmuch as it approaches conductivity water in resistance, and that from certain natural ices may well be likewise.

It is not unlikely, too, that the rare mineral native mercury is not infrequently almost spectrographically pure.

Of the ninety-two elements, two, 85 and

87, have yet to be isolated; six — Ac, Pa, Po, Ra, Ma, and Re — occur in too low a concentration in minerals to register. Of these six, the first four are radioactive. Fourteen more do not register: H, N, O; A, He, Kr, Ne, Rn, Xe; Cl, Br, I; S, Se. Two more, C and F, emit few if any lines in the usual sense, but yield bands under certain conditions which can be recognized. Of the remaining seventy elements, nine, including Sm and eight rare earths, Dy, Eu, Ho, Il, Lu, Tb, Tm, and Yb, are not likely to be encountered in a sufficiently high concentration to cause serious confusion. Nd and Pr always occur together and are therefore listed by the symbol of their former joint name "didymium," Di. Thus, we have reduced the list of special and practical interest to the spectrographer in the qualitative examination of minerals to the sixty in Table I.

The three elements in parentheses require a shift of range, however. B must be sought a bit further down in the ultra-violet (2497, 2498), but amounts of elements such as Ca, Li, and Rb that would be required to identify a mineral positively would be within the range. If a negative identification arising out of the absence or extremely minute amount was in question, one would naturally resort to a panchromatic or plate sensitive to extreme red. Cs (4555, 4593, 4604) lies out in the blue, and here, too, will be found the head of the CaF_2 band (5291) by means of which F may be detected even in low concentrations (0.01 per cent).[4]

There is a special and intimate relationship between *fluorite* and fluorine in nature, for, when the former is subjected to radiation by radioactive elements, some of the fluorine atoms are actually displaced from the molecule and become entrained as gaseous fluorine. At the same time, the *fluorite* is colored dark purple so that it appears black. If this variety is fractured or cut, the free fluorine is released and instantly ozonizes the surrounding air to a

TABLE I

SIXTY ELEMENTS OF SPECTROGRAPHIC IMPORTANCE IN THE ARC DETERMINATION OF MINERALS

	Atomic No.		Atomic No.		Atomic No.		Atomic No.
Ag	47	(Cs)	55	Li	3	Sc	21
Al	13	Cu	29	Mg	12	Si	14
As	33	Di {Nd	60	Mn	25	Sn	50
		{Pr	59				
Au	79	Er	68	Mo	42	Sr	38
(B)	5	(F)	9	Na	11	Ta	73
Ba	56	Fe	26	Ni	28	Te	52
Be	4	Ga	31	Os	76	Th	90
Bi	83	Gd	64	P	15	Ti	22
C	6	Ge	32	Pb	82	Tl	81
Ca	20	Hf	72	Pd	46	U	92
Cb	41	Hg	80	Pt	78	V	23
Cd	48	In	49	Rb	37	W	74
Ce	58	Ir	77	Rh	45	Y	39
Co	27	K	19	Ru	44	Zn	30
Cr	24	La	57	Sb	51	Zr	40

point which may be disagreeable or almost intolerable. Hence, miners who encounter this mineral in Germany term it "*Stinkstein*" whereas the mineralogist knows it as *antozonite*.

It is felt that, in the main, Putnam's idea is an admirable one, but that revision and expansion to meet spectrographic needs will be very helpful. A folding chart does not lend itself to ready reference, 80 per cent of the space being unoccupied as well, and the number of elements could either be reduced to those of spectrographic importance, or they could be separately indicated.

It is provisionally proposed, therefore, to tabulate the minerals listed in page format, keyed to the basic chart, but supplemented with the names, spectral constituents, formula, color, density, and other useful determinative data, and a type table is submitted (Table II).

It will, of course, be necessary to in-

corporate those minerals described in the interim since July, 1924; this could readily be done by reference to Spencer's lists of new minerals.[5]

THE DETERMINATION OF MINERALS

The first task of the spectrographer is to determine the most conspicuous elements present and arrange them in what appears to be the relative order of importance. Search should finally be made for unusual and rare "trace" elements whose presence or absence may prove of significance.

If only one major element is found other than a native one, it becomes necessary to determine what the electronegative element may be. In such instances, the presence (or absence) of unusual or extraneous elements may often be helpful. For example, suppose that only Zn has been found the major base. The question then arises, is the mineral *zincite* (ZnO), *smithsonite*

TABLE II

Abcissa Element	Ordinal Element	Putnam Index No.	Name	No. of Primary Spectral Constituents	Primary Spectral Constituents	Formula	Common Color	Rensselaer Polytechnic Institute Tables[2]	
								Density	Hardness
Mg	P	1480	Newberyite	2	Mg, P	$HMgPO_4 \cdot 3H_2O$	White	2.10	3–3.5
Mg	P	112	Bobierite	2	Mg, P	$Mg_3P_2O_8 \cdot 8H_2O$	Colorless; white	2.41	2
Mg	P	781	Struvite	2	Mg, P	$NH_4MgPO_4 \cdot 6H_2O$	White; yellowish	1.65–1.72	2
Mg	P	1316	Hannayite	2	Mg, P	$H_4(NH_4)_2Mg(PO_4)_2 \cdot 8H_2O$	White; yellowish	1.893	soft
Mg	P(F)	869	Wagnerite	2(3)	Mg,P(F)	$(MgF)MgPO_4$	Yellow; grayish; flesh-red; greenish	2.985–3.14	5–5.5
Mg	P(B)	513	Lünebergite	2(3)	Mg,P(B)	$3MgO \cdot B_2O_3 \cdot P_2O_5 \cdot 8H_2O$	Colorless	2.05	......
Mg	P(Ca)	381	Hautefeuillite	3	Mg,P,Ca	$(Mg,Ca)_3P_2O_8 \cdot 8H_2O$	Colorless	2.435	2.5
Zn	P	406	Hopeite	2	Zn, P	$Zn_3P_2O_8 \cdot 4H_2O$	Grayish white	3.03	2.5–3
Zn	P	619	Parahopeite	2	Zn, P	$Zn_3P_2O_8 \cdot 4H_2O$	Colorless	3.21–3.31	3.5–4
Zn	P	930	Tarbuttite	2	Zn, P	$Zn_3P_2O_8 \cdot Zn(OH)_2$	Colorless, pale yellow, brown, red, green	4.12–4.15	3.5–4
Zn	P	1171	Spencerite	2	Zn, P	$Zn(PO_4)_2 \cdot Zn(OH)_2 \cdot 3H_2O$	White	3.123–3.142	3

($ZnCo_3$), *Hydrozincite* (basic zinc carbonate), or *sphalerite* (ZnS)? The presence of In, Ga, and Ge would indicate that *sphalerite* is most likely, whereas In and Ge together would be more indicative of *smithsonite,* but strong lines of Mn would point to *zincite.*

Naturally, however, the spectrograph is at a disadvantage in distinguishing between polymorphs such as *calcite* and *aragonite, pyrite* and *marcasite,* or *rutile, brookite,* and *octahedrite,* but fortunately, simple criteria are usually available which will enable one to make a distinction in such instances.[2]

Substances such as *limonite, hematite, magnetite,* and *siderite,* all of which would register only Fe as the major element, might seem puzzling until one recalls that their streaks on unglazed porcelain are, respectively, yellow, red, black, and colorless.

It should be emphasized that even a complete chemical analysis is not always sufficient to identify a mineral precisely (for instance, members of the garnet group), so that unavoidably there are limitations to the interpretation which can be made from some plates.

A knowledge of mineralogy is certainly very helpful in making determinations and tends to make them easier and quicker, but a chemist or a physicist with access to the literature should be able to reach the same decision in many cases albeit he may be longer in doing it and necessarily must be more cautious.

In any event, one's skill improves with practice, and it is an excellent idea not only

first to study known species of relatively simple composition, but at the same time to build up a collection of useful controls from known localities for reference purposes.

The native elements, of course, will offer no difficulty, but because of their relative scarcity are not often encountered. Nevertheless, the unexpected may happen. Some months ago, a sample of alluvial *cassiterite,* native tin oxide, was being ground preparatory to analysis, when some small malleable particles were found which our spectrograph disclosed to be essentially only tin. Search of the literature disclosed that this metal is perhaps the rarest of the native elements, repeated reports of its existence being considered not unimpeachable for many years.[6]

In the eight mineral classes, the sulfides, selenides, chlorides, bromides, iodides, oxides, carbonates, nitrates, sulfates, organic salts, and hydrocarbons will leave no spectrographic evidence of their nature save that furnished by the bases contained, ammonium excepted. The foregoing refers to graphite electrodes. However, these deficiencies are not so much of a handicap as might at first be conjectured, for obvious reasons.

RAPID DETERMINATION OF CONFUSING COMMON MINERALS

It frequently happens that inspection and simple tests have made it virtually certain that a specimen may be either of two species closely resembling each other. In such instances, the spectrograph can give a speedy and conclusive answer.

Graphite	C		Quartz	SiO_2		Calcite	$CaCO_3$
Molybdenite	MoS_2		Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$		Dolomite	$MgCO_3$
Pyrite	FeS_2		Barite	$BaSO_4$		Actinolite	
Chalcopyrite	$CuFeS_2$		Barytocelestite	$BaSO_4 + SrSO_4$	6	Green tourmaline	B, F

GROUP STUDIES

Certain important minerals fall into natural groups the members of which grade into one another. The compositional study of such groups always makes a very interesting comparison, and it is often possible to identify the individual species. A good example is furnished by the micas:

Muscovite	K
Phlogopite	KMg
Biotite	KMgFe
Lepidolite	KLi
Zinnwaldite	LiFe

rarity or from other reasons, we can only briefly touch on certain other interesting possibilities inherent in the spectrographic method of investigation. Among these may be mentioned looking for new minerals of the rarer elements, locating new occurrences of species already known, and differentiating two minerals or ores of similar gross composition as coming from different deposits.

For example, a large electrical manufacturing concern wished to have an independent source of *pollucite*, the chief ore of
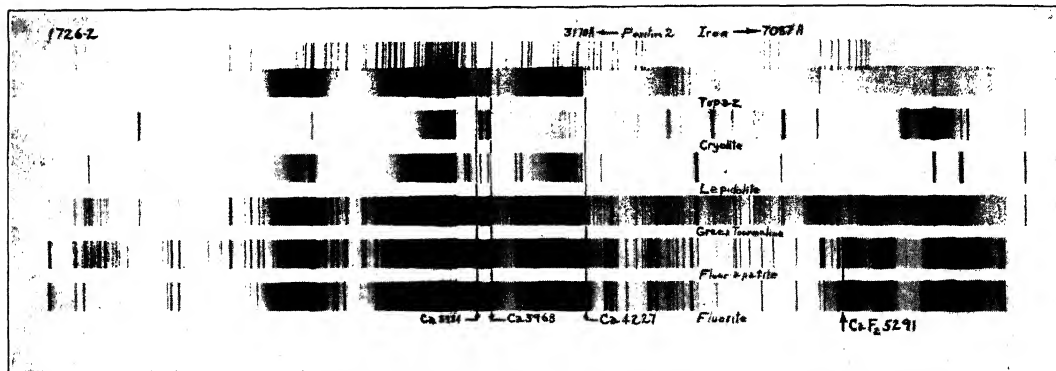
Fig. 1

In 1930, one of us utilized the Lundegårdh method of spectrographic analysis[7] in which a definite volume of solution is atomized through a high-temperature flame of compressed air and acetylene. Out of curiosity, fragments of certain minerals were held directly in the flame with pincers for several minutes, and it was found that numerous elements were sufficiently volatile to be recorded. The result of one such investigation on the determination of rare alkalies in lepidolite and allied micas is shown in Fig. 1.

As determinative mineralogy has been our main concern particularly where the material is very limited because of its

cesium, containing up to 34.68 per cent of the element much used in radio vacuum tubes. The only deposits of consequence then known were in Maine, but there was every reasonable expectation that this mineral should occur also in the pegmatites of the Black Hills of South Dakota. Unfortunately, it is a disarmingly inconspicuous species. A characteristic specimen presented to several mineralogists and geologists for identification was consistently mistaken for quartz, which it resembles very closely.[8]

Systematic spectroscopic examination of minerals from many mines in the region was accordingly stimulated, and some time

later a deposit of *pollucite* was located at the Tin Mountain Mine near Custer, South Dakota, from which a carload of cesium ore was shipped east to be worked up into cesium chloride.[9] As a result of this spectroscopic prospecting, also, a new variety of mica, *cesium biotite,* was discovered in the same vicinity, analyzing 3.14 per cent of cesia.[10]

The number of minerals containing germanium as an essential constituent is very limited, and all are very rare. One of the most recent and probably the richest is the complex copper ore *germanite* from Tsumeb, Southwest Africa, which contains 8.7 per cent of Ge and 0.76 per cent Ga.[11] The late Professor Charles James of the University of New Hampshire published a note with regard to the occurrence of germanium in a copper mineral from the far west rich in germanium, without giving its exact occurrence. In a private communication to one of us he expressed the opinion that it was not *enargite,* copper sulfarsenate, because the percentage of germanium was much too great. Here, then, is a clue which might lead the curious spectrographer not only to a new source of this rare element but even to a new mineral.

Again, in recent years spectrographic examination has disclosed that beryllium is more widely distributed than was formerly supposed, [12, 13] and present in minerals not usually supposed to contain this element.[7]

Conclusion. We have not attempted to persuade ourselves that the system as set forth will prove to be a perfect one. Nevertheless, the very imperfections of a scheme such as we have formulated have often proved a stimulus to its development rather than a detriment to its practical usefulness. If, then, we should have succeeded in reviving an interest in determinative mineralogy on the part of chemists and spectrographers, calling attention to the aid which may be rendered by an instrument which is becoming more familiar, we shall feel amply rewarded.

REFERENCES

1. P. C. PUTNAM, "A Chart Showing the Chemical Relationships in the Mineral Kingdom," Wiley & Sons (1925).
2. J. L. ROSENHOLTZ and D. T. SMITH, "Tables and Charts of Specific Gravity and Hardness for Use in the Determination of Minerals," Rensselaer Polytechnic Institute, Eng. & Sci. Series 34, Troy, N. Y. (June, 1931).
3. L. J. SPENCER, "Specific gravities of minerals: an index of some recent determinations," *Mineralog. Mag.,* 21, 337–365, (December, 1927).
4. J. PAPISH, L. E. HOAG, and W. E. SNEE, "Spectroscopic Detection of Fluorine," *Ind. and Eng. Chem.,* Anal. Ed., 2, 263–264 (July 15, 1930).
   H. V. CHURCHILL, "Occurrence of Fluorides in Some Waters of the United States," *Ind. and Eng. Chem.,* 23, 996-998 (September, 1931).
5. L. J. SPENCER, Lists of new mineral names: 10: *Mineralog. Mag.,* 20, 444–477 (September, 1925); 11: *ibid.,* 21, 556–582 (September, 1928); 12: *ibid.,* 22, 614–632 (September, 1931); 13: *ibid.,* 23, 624–640 (September, 1934); 14: *ibid.,* 24, 601–628 (September, 1937).
6. J. W. MELLOR, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 7, 283 (1927).
7. H. LUNDEGÅRDH, "Die quantitative Spektralanalyse der Elemente," G. Fischer, Jena (1929).
8. E. E. FAIRBANKS, "The Importance of Pollucite," *Am. Mineral.,* 13, 21 (January, 1928).
9. J. P. CONNOLLY and C. C. O'HARA, "The Mineral Wealth of the Black Hills," p. 261, Rapid City, S. D. (May, 1929).
10. F. L. HESS and J. J. FAHEY, "Cesium Biotite from Custer County, South Dakota," *Am. Mineral.,* 17, 173 (May, 1932).
11. F. W. KRIESSEL, *Chem. Z.,* 48, 961 (1924).
12. C. PALACHE and L. H. BAUER, "On the Occurrence of Beryllium in the Zinc Deposits of Franklin, N. J., *Am. Mineral.,* 15, 30 (January, 1930); H. S. WASHINGTON, "Beryllium in Minerals and Igneous Rocks," *ibid.,* 16, 37 (January, 1931).
13. C. PALACHE. "On the Presence of Beryllium in Milarite." *ibid.,* 16, 469 (October, 1931).

QUANTITATIVE ANALYSIS BASED ON SPECTRAL ENERGY*

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The carbon arc behaves like a small furnace, vaporizing the various constituents of a sample placed in it in order of boiling points. When intensity is taken as a measure of concentration of some element, as advocated by Gerlach and Schweitzer, large errors may result, because the peak of the volatilization period may shift on the time axis, owing to the influence of other constituents present in the sample. But if the total energy of emission of the element in question (the intensity integrated over the time of emission) be taken as a measure of concentration, this difficulty should be overcome.

The arc is regarded as a furnace which volatilizes the elements it contains into the arc column, where they are excited to emit their spectrum and then pass out into the surrounding atmosphere. According to this view, there should be a quantitative relation between the number of atoms passing through the arc column (and hence the weight of the element) and the spectral energy emitted. If we assume the simplest case, that the relation is linear, then the equation which expresses this is

$$m = k \int I dt$$

where m is the mass of the element in question, I the intensity for any interval of time dt, and k a proportionality constant.

In order to check this idea experimentally, suitable amounts of various samples, whose composition was accurately known, were weighed out on a microbalance, transferred to the cores of graphite electrodes, and completely volatilized in the arc. The photographic plate performed the integration required by the equation. In order to convert plate response into relative energy, each plate was given a graduated series of exposures to a mercury lamp whose output was constant and reproducible. Due precaution was taken to collect an aliquot of the emitted light by means of a special condensing system, and to minimize the photographic reciprocity error.

The element whose emission was measured was calcium. The samples were nine minerals and rock products whose Ca content (as CaO) varied from 0.21 to 34.02 per cent. The composition of these samples varied greatly, in order to determine the effect, if any, of the base material on the emission. The samples were run in quadruplicate, giving 36 experimental points.

When the energy of emission (in arbitrary units) was plotted against weight of CaO consumed in the arc, a straight line

was obtained, all the measured values falling consistently on the curve. The average deviation was found to be 8.3 per cent, and the maximum deviation was 18 per cent. The experimental result therefore agreed with the equation given above.

This linear relationship between weight of element and its spectral emission can readily be applied to quantitative analysis. As the concentration C is the ratio of element to total sample, the above equation becomes

$$C = \frac{m}{M} = K \int \frac{I\,dt}{M}$$

where M is weight of sample. All the factors are known except the constant k, which can be determined once for all by measuring the emission of analyzed samples in the approximate concentration range of the unknowns. This constant is a function of the experimental set-up and is apparently independent of the base material of the sample.

The method outlined here is particularly adapted to research work or occasional samples, as the standardization requires little time. It is much more versatile than the procedures based on an internal standard, since the restrictions imposed by the internal standard element are absent. The accuracy is of the same order as the best of present methods.

ANALYSIS OF MATERIALS BY FLUORESCENT METHODS

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A brief account of applications of fluorescence methods to the rapid qualitative analysis of materials is of interest in connection with spectroscopic discussions. One of the most comprehensive books published on this subject was written by J. A. Radley and Julius Grant, "Analysis in Ultra-Violet Light," and published by D. Van Nostrand Company. Many of the examples cited are taken from this book.

The technique of fluorescence analysis is particularly adaptable to a great variety of cases that cannot be satisfactorily handled by the spectroscope, such as rapid examination for the adulteration of butter or for bacterial growths on meats in storage. Although the general method has been applied to many lines of investigation, it is not applicable in all. Perhaps a discussion of the phenomena of fluorescence and phosphorescence will make the reason for this clear.

Certain substances, when exposed to invisible ultraviolet light, will glow with fluorescence of a characteristic color. It may be any color and shade from red to violet, depending entirely on the nature of the irradiated substance. If the glow persists after the sample has been removed from the exciting ultraviolet light, the phenomenon is called phosphorescence.

If the fluorescence produced is characteristic of the substance irradiated, it may serve as a means of analysis. For ordinary work it is usually sufficient to note the intensity and color. The specimen is observed by placing it in a shielded viewing box and illuminating it with a filtered quartz mercury lamp, or by working in a dark room. Often the results are obtained in conjunction with chemical tests where the filter or filtrate is irradiated, or where a chemically treated surface is irradiated, the chemical treatment forming fluorescent compounds if the element in question is present. For a more critical examination the fluorescent light may be examined with a spectroscope.

The above is not applicable to every case since many substances do not fluoresce. Also highly fluorescent impurities of variable amount may easily contaminate the sample, or it may occur that the fluorescence of the material in question depends greatly on its previous history. Occasionally this last point may be turned to advantage to determine the previous history of the sample.

If one wishes to test the possibility of a fluorescence analysis of a material, he must conduct a period of preliminary research to determine first whether the test can be controlled and to establish his standards. If it is found that the impurity in question causes a definite type of fluorescence which either does not vary greatly with other con-

ditions, or varies in a perfectly definite way, then fluorescent light may be used as a means of analysis. Standards may be made up of known percentages of the material in question for comparison with the unknown. In this way a rough qualitative estimate of percentages is possible. All this sounds very simple, and for that reason I cannot overemphasize the importance of a thoroughgoing investigation of the effects on the fluorescence of all possible varying factors. Only after these investigations have been made and the dependence of the fluorescence on the extenuating circumstances is known may one adopt with confidence the use of fluorescence analysis in a particular case.

For concrete illustrations of the uses which have already been made of this type of analysis I quote examples from a number of fields of science and industry.

Agriculture. Fertilizers can be examined.

Four kinds of wheat can be distinguished.

Bacteriology. Many species of bacteria have characteristic fluorescence; in addition, different strains of the same species show different shades.

Bacterial contamination of tobacco can be detected, even through the cigarette paper.

Certain mold fungi can be distinguished.

Molds and bacterial growths on meats and fish are easily detected, in connection with studies on their keeping properties.

Botany. In many instances the cell structure of plants is clearly shown; for example, if a microtome section cut through the stalk of a certain plant is immersed in water, the peripheral cells, which are filled with wax, glow with a bright yellow color. The cells on the outer surface fluoresce with a blue color, and the chlorophyll glows with its characteristic red color; the center of the section, however, has a few or none of these red-fluorescent cells.

Constructional Materials and Glass. The products of the silicate industry and the weathering of rocks may be tested.

Drugs. There are numerous applications, both to powders and solutions; also to greases, fats, and oils. Mineral greases are readily detected in ointments and mineral oils in other oils. A sample of oil supposed to be genuine seal oil gave an intensive blue fluorescence, showing the presence of a considerable amount of mineral oil.

Foods and Food Products. Five per cent refined olive oil can be detected in virgin oil as against a minimum of 65 per cent by direct observation. Fifteen per cent of margarine is easily detected in butter. Five per cent of artificial fats can be detected in butter. The age of the butter and its degree of rancidity can be gauged to some degree from the extent of the change in the color of the fluorescence from yellow to blue. Forty per cent of Czechoslovakian lard, and 10 per cent of Dutch lard, are detectable in American lard. The yellow fluorescence of milk preserved in formaldehyde persists for months. Separated fat from artificial cream has a blue fluorescence, whereas fat from genuine cream shows a yellow fluorescence. The age of eggs may be determined roughly; also removal of the mark of origin from eggs can be detected. Wheat and rye flours show a clear bluish fluorescence while barley and potato flours appear white and grayish-brown respectively. Oils, butter, milk, lard, eggs, cocoa, preservatives, spices, mushrooms, flour, vinegar, wine, liquors, sugars, jams, pulps, honey, and essential oils can also be tested by fluorescence.

Fuels and Lubricants. It is possible to distinguish between many types of bitu-

mens, asphalts, tars, etc., both natural and artificial, with a rapidity unobtainable by the usual chemical and physical methods.

Leather and Tanning. Artificial tanning agents can be distinguished from natural tanning agents, and from mixtures of the two.

Legal and Criminological Work. In connection with customs examinations, body marks, documents, inks, fingerprints, stains, seals, and adhesives, the method offers possibilities.

Minerals and Gems. Real and artificial gems, such as sapphires and pearls, can be distinguished.

Museum Work. The method is valuable in establishing the authenticity of paintings, documents, fossils and remains, and ceramics.

Organic and Inorganic Chemistry. Chemical applications are numerous. It is claimed that 10^{-5} gram of arsenic can be detected. Also compounds in mixtures, etc., may be identified.

Paints and Varnishes. The method has wide application; oils, waxes, resins, pigments, and drying agents can be examined. Fading and ageing tests can be carried out.

Paper and Cellulose. The method is valuable for comparative work, for control of purity, and for processing of raw materials.

Rubber. Routine testing and the determination of source and quality of materials can be expedited.

THE SPECTROGRAPH AS AN ANALYTICAL TOOL FOR MEDICAL USE

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The papers which have been presented at previous conferences have dealt largely with one subject, with the emphasis on

FIG. 1. Optical Bench with Accessories.

quantitative analysis. It was felt that a description of inexpensive spectrographic equipment applicable to the great diversity of problems encountered in our laboratory would be of interest to many commercial, educational, and pharmaceutical laboratories.

The apparatus is of a very simple type, which increases the adaptability to different problems. The main item is a medium quartz spectrograph in conjunction with which a number of accessories may be used (Fig. 1). An optical bench, carrying an arc or spark stand, one spherical quartz lens, one cylindrical quartz lens, and a motor on which may be placed a number of types of log sectors or a variable

sector disk, is attached to the spectrograph in front of the slit. This arrangement allows a great latitude of set-up according to the demand of the problem. The type and number of lens, the log sectors, and the source, arc or spark for solid or liquid samples, may be easily interchanged. It has been found that for quantitative analyses the use of a log sector or a stepped sector, in conjunction with a microdensitometer, is very useful for larger quantities of material; a microdensitometer alone, using a photographic wedge, gives more reproducible and accurate results for the lower determinable ranges.

This bench, with its accessories, is entirely replaceable by a bed to which is
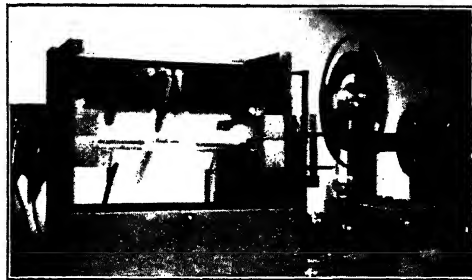
FIG. 2. Hydrogen Discharge Tube and Photometer.

rigidly fixed a single sector photometer and hydrogen discharge tube (Fig. 2). The high-voltage electrical and water out-

lets are then directly behind the tube within easy reach. As the tube, cell holders, sector, and optical system are rigidly attached to the bed, the system is easily aligned with the spectrograph. This is accomplished by four set screws which, once the bed is aligned and the screws locked in position, will always after future changes place the bed optically in line. Thus it is possible to change from a set-up for emission analysis to one for absorption work, or vice versa, in two or three minutes and have the instrument ready for use. It was not found necessary to expose a plate to determine the correct adjustment, for this has been found to be reproducible.

The 110-volt alternating current for operating a 5000-volt transformer is obtained from a motor-generator set which is controlled from a panel adjacent to the instrument, from which different voltages may be selected (Fig. 3). Variable direct current may also be obtained here. Relays, transformers, and resistances are placed beneath tables out of the way. As a photographic darkroom is necessary, part of the main room has been walled off and supplied with sink, enlarger, and other accessories.

The many problems that are referred to the laboratory generally fall into two classes. In the first, the chemical composition of the medicinal product is probably known, for the manufacturer has already made an investigation, but the laboratory must check the work that has been done previously, prepare a series of tests that will standardize the product, and determine the presence and amount of impurities. Of course, preparations consisting of mixtures may make the investigation rather complicated.

One of the products which has recently been accepted by the Council on Pharmacy and Chemistry of the American Medical Association and for which standards have been prepared is riboflavin, also known as vitamin B_2, or lactoflavin. Among the
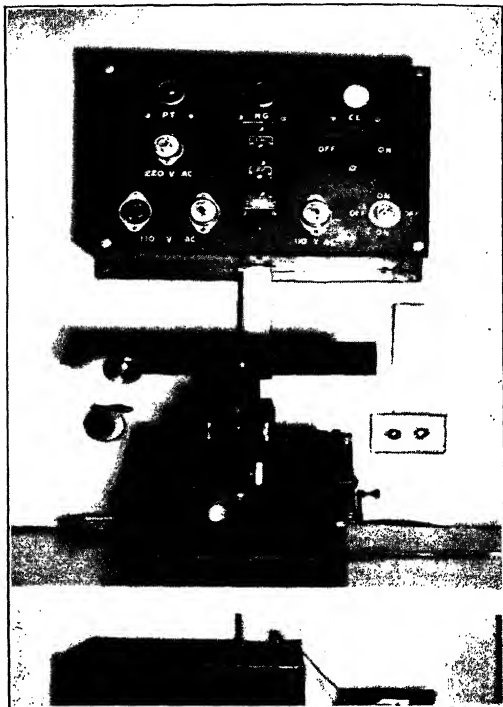
FIG. 3.　Electrical Control Panel and Microdensitometer.

standards to which this product must conform is that it shall have absorption maxima at 445, 372, 269, and 225 millimicrons, and that a 0.005 per cent solution in water shall have an extinction coefficient of 1.45 to 1.65 at 445 millimicrons. The curve for this compound is here shown, for it is the first time that a spectrographic standard has been accepted for a medicinal product (Fig. 4).

In the second type of problem, nothing is known about the product; thus a complete qualitative and quantitative analysis

is necessary. Most of this work is submitted by the Bureau of Investigation and is concerned with the "patent medicines," that is, those with secret or semi-secret formulas. Many of these are rather complex mixtures of ingredients. In this con-
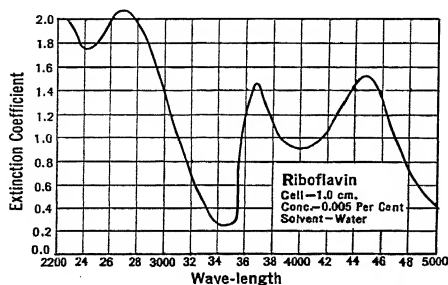

Fig. 4. Absorption Curve of Riboflavin.

nection, a spectrograph renders invaluable service, for in a few minutes all the metals, whether present in large quantities or in traces, may be identified without resorting to the time- and money-consuming chemical methods. In fact, we have practically omitted the chemical qualitative analysis except as a check. In dealing with such products as medicinal dyes, compounds of the transition elements, vitamins, and hormones, the absorption equipment is of great value. The list of compounds which have been foisted upon the public includes the majority of the elements, many of which, such as gold, thallium, radium, and lithium, are not encountered in common chemical qualitative analysis. Here the most useful side of the spectrograph is applied, for exact qualitative analysis of from ten to fifteen materials may be made in an hour, and a permanent record of the analysis is obtained. This permanency of records is extremely important in the event of lawsuits, which play a rather important role in the work.

With the aid of a spectrograph, extremely small but nevertheless therapeutically

significant amounts of metals may be detected, whether they are present as impurities or as physiologically active ingredients, such as zinc in "crystalline insulin" or protamine zinc insulin. In one case, a salve claimed to contain mercury in organic combination baffled all attempts to detect the mercury chemically. It took but a short time to show that mercury was present but in an amount much smaller than that claimed.

With the equipment it is also possible to make quantitative determinations. Owing to the fact that ferrous metals are seldom encountered in medicinal products, it is possible to use an instrument which does not have an extremely high dispersion and still obtain acceptable results.

This apparatus also meets many other needs in the laboratory. It is the purpose of one department of the American Medical Association to examine equipment for physical therapy. Included in this are various types of therapeutic lamps and ultraviolet-ray equipment. It is possible to study the spectral distribution of the emissions from these instruments and to compare them with a standard source with the aid of a quartz reflecting prism attached to the photometer.

A number of instances have been encountered in which it was necessary to test a portion of a patient's skin for the deposition of certain metals. Using a spectrograph for the test it has been found that the removal of sufficient material will not disfigure the patient, even if the biopsy specimen is from the face.

Thus, in our laboratory, we have found that inexpensive spectrographic equipment has enabled us to solve a great variety of analytical problems which had previously proved baffling; saves valuable time, samples, and reagents; and furnishes an excellent means of standardizing certain medicinal products.

CHARACTERISTICS OF SPECTROSCOPIC LIGHT SOURCES

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Anyone who has read the literature of quantitative spectroscopy will certainly have been struck by the diversity of light sources used and by the divergence of opinion regarding their relative excellence. One hears of flames, of a-c and d-c arcs, at both high and low voltages, and of condensed sparks of various voltages and frequencies — unidirectional, oscillating, and damped. The material under investigation may be in the form of a solution which may be introduced into the discharge by any one of several methods; or in solid form; or in the form of a powder or liquid placed in a cavity in a graphite electrode, with or without a binder, a stabilizing buffer, or a reference element. Exposure may be preceded by a " warm-up " operation of the source, may or may not continue to exhaustion of the sample, and may utilize light from every part or from a definite portion only of the source. Some investigators believe that one light source is adequate for all problems; others believe that the selection of a suitable source is the first step in attacking a new analysis.

Certainly, in the selection of a source, the test of experiment is the final one, for no source is useful which will not make possible adequately sensitive and accurate analysis. There are, however, certain general characteristics of sources that may well be considered. The ideal source for quantitative spectroscopy would be one in which all elements in the matrix enter the discharge, diffuse through it, and are excited to radiation at a uniform relative rate, regardless of boiling points, atomic weights, vapor pressures, or excitation functions; or of variations in the discharge conditions; or of the time. Fortunately it is not essential to have such an ideal or absolute source.

Much has been written about the various excitation processes in different types of discharge. A simple concept, however, seems adequate for our discussion. It appears fairly certain from the work of Ornstein, Mannkopf, and others that excitation in any of the ordinary spectroscopic sources may be considered to be thermal. The temperatures in arcs vary from 3500°-8000° C, and in sparks, up to as much as 10,000° C.

The intensity of a spectral line radiated by a hot gas is described by

$$I \backsim N\,Pe^{-\Delta E/KT}.$$

(N, number of atoms per unit volume; P, transition probability; ΔE, energy difference between initial and final levels; K, the Boltzmann constant; T, the temperature).

In quantitative spectroscopy, by an internal standard method, the analysis is based on a determination of the relative

intensities of a line of the substance present in unknown concentration and of a line of the reference element. For successful analysis, this ratio must be highly reproducible. Obviously, any cause of variability that affects the ratio of N of the standard to N of the unknown element, or that affects T, is certain to affect adversely the ratio of intensities and so the accuracy of analysis. An investigation of the behavior of the instantaneous value of T in spectroscopic light sources would be of fundamental value. However, a temperature determination involves a long enough time interval to make it possible to obtain measurable line intensities, and, therefore, such a determination cannot follow rapid fluctuations. But from the work in Ornstein's laboratory we know that the temperature of an a-c carbon arc varies with

FIG. 2

and upon the rate at which energy is lost by radiation. All these factors may be significantly influenced by variations in the content of the column. Thus Elenbaas,[2] Fig. 2, has shown that the effect upon a mercury-vapor discharge of the addition of small percentages of cadmium is a marked decrease in temperature. At the same time the intensity of the Cd lines is altered with increasing Cd content in the arc by three effects: (1) increase in the number of Cd atoms, which increases the number of radiating atoms; (2) decrease in the temperature of the gas because of increasing energy loss; (3) increase in the self-absorption. The second and third effects act oppositely to the first and tend to produce a saturation effect.

Accuracy in spectrographic analysis demands then a light source in which the average values of N, the number of atoms per cubic centimeter in the discharge, and of T, the temperature of the discharge, are very nearly constant; but other factors, such as the sensitivity required, the form of the material to be investigated or its availability, may, of course, influence the choice. We come, then, to a discussion, in the light of these factors, of some of the more common sources and of some practical experience with them.

FIG. 1

the cyclic variation in energy input, but has a phase lag. That this effect is relatively great may be seen from Fig. 1, which shows (a) the temperature, and (b) the energy variation with time in a 50-cycle arc.[1] Obviously, it is essential for satisfactory analytical results with any source to have either constant energy input or constant average energy input over the time of exposure.

The temperature attained in the discharge depends also upon the specific heat and the conductivity of the gas column,

In assembly and operation, the simplest

source, apart from flames, is the d-c arc. Because of its relatively low temperatures, the excitation is chiefly to a few of the lower terms, and the result is high sensitivity for metals which are present in the electrodes in low percentages. Accordingly, the arc is one of the most useful sources for the detection of very small amounts of impurities, and for the inspection of materials. On the other hand, the d-c arc is one of the most erratic and variable of sources and one of the most difficult with which to obtain accurate results. Some of the reasons for this variability are easily understood.

The arc column consists of a bright, hot, central core surrounded by an envelope or halo of cooler gas. At the cathode, the discharge goes to a small, intense cathode spot, which depends, for size, on such factors as the cathode material, current strength, and gas atmosphere, and which must supply the electron emission to maintain the arc. The chief source of variability in the arc seems to be the wandering of the cathode spot with accompanying marked instability of the arc, which sputters and may even hiss if the fluctuations are rapid enough. We have examined both the current and potential difference of such arcs with an oscillograph. Extremely rapid, spasmodic, and quite irregular variations of as much as 50 per cent, of both current and voltage, appear, in opposite directions. Such fluctuations, of course, are concomitant with fluctuations in the release of electrode material and in the arc temperature. The movement of the cathode spot entails variations in the temperature of the disengaging spot and in the time of disengaging from one spot, and since elements with different boiling points enter the discharge at different rates and time intervals,[3] there must follow fluctuations both in the total and in the

relative number of the different kinds of atoms entering the discharge. The variation in N affects both factors in our intensity expression; the variation in I and V affects T. The arc varies in intrinsic brilliancy and in total intensity, as well as in relative distribution of intensity among the different spectral lines. These variations are easily apparent.

Quantitative analysis with a d-c arc is based on the hope that over the whole exposure the variations will average out in a fairly repeatable manner. Often results from two or more exposures are averaged. If the material is placed in a cavity in a graphite electrode, it may be burned to exhaustion,[4] in the hope that the total number of atoms may emit in a more uniform manner than some part. In any case, however, variations in the rate of release of material affect T and, therefore, relative as well as absolute intensities. Our experience with attempts to analyze alloy cast iron with a d-c arc has been discouraging. Iron is, no doubt, an especially unfavorable material in an arc. However, high accuracy has seldom been claimed for analysis performed with a d-c arc.

One seeks, of course, some way to stabilize the wandering of the cathode spot and the fluctuations in arc current. An arc to accomplish this purpose for iron analysis, described by the authors,[5] uses an upper graphite cathode and rotating lower iron anode, which is hot enough to throw off droplets of molten iron and so to present continually a fresh surface to the arc. Results are considerably better than with the small arc.

We have tried also a high-voltage d-c arc with a large stabilizing series resistance. The accuracy in iron analysis is better than with the 220-volt arc but not so good as in the rotating type described above.

Voltage fluctuations occur, together with wandering of the cathode spot.

Another attack on the arc problem is that of Duffendack and Thompson in their use of a high-voltage a-c arc.[6] It has been used by various investigators for fluids and solutions, with graphite electrodes on the tips of which a sample is dried. We have adapted it to metallic electrodes in the analysis of automobile body sheet steel, because of its high sensitivity and small consumption of material. Oscillograph observations show a nearly sinusoidal variation of the current, while the voltage (Fig. 3) shows peaks at the
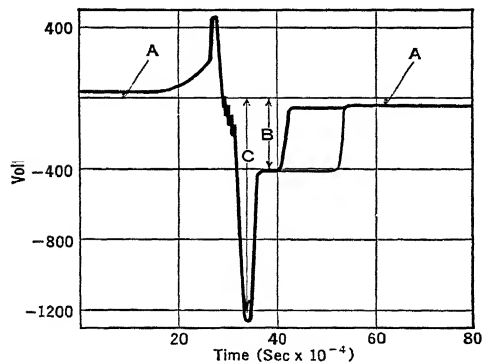
FIG. 3

break and at the re-ignition of the arc. Each new half cycle starts with a glow, probably with some explosive release of electrode material, as in a spark discharge, followed by a transition to an arc. The wandering of the cathode spot is controlled or regularized in that it is forced to re-establish itself at each half cycle. The result is a form of arc which is considerably more reliable than the simple d-c arc.

The a-c arc may be thought of as an uncondensed spark with a sinusoidal current of low frequency and of constant amplitude fixed by the applied voltage and resistance. In the condensed spark there is, at each transformer half cycle, an oscillatory discharge with a frequency which may be anything up to hundreds of thousands of cycles per second, and with a current which may reach an amplitude of hundreds of amperes in the first cycle and is damped rapidly in succeeding cycles. The behavior of voltage and current is much like that in the a-c arc, but with much higher frequency and with a decrement of the current which depends on the rate at which energy is lost in the spark circuits and from the spark itself. The number of oscillations in the spark train at each transformer half cycle depends on this decrement and also on the initial energy in the condensers, i.e., the voltage at which the initial breakdown occurs. Studies of the spark with a rotating mirror show that material is released simultaneously from each electrode — presumably by ion bombardment — and moves out into the spark gap as a luminous streamer. The succeeding arclike discharge is in this electrode vapor and radiates the spectrum of the electrodes.

It is evident that the energy input to the spark must oscillate with the spark frequency and with a diminishing amplitude, and that, therefore, there must be an oscillating temperature with corresponding decrement. However, an average temperature for the spark may be determined, as has been done by Langstroth and McRae,[7] who found temperatures of 8000° to 10,000° C for discharges between a point and a plane electrode. For accurate analysis it is desirable to have the same voltage (energy) at the initiation of each spark train and the same decrement of current in each train. In terms of our equation, this insures uniformity of N because of equal initial energy used in re-

leasing electrode material, and it insures a uniform average T because of uniform maximum energy and uniform decrement. A few seconds or minutes of pre-sparking before exposure serves to outgas the electrodes, to form an oxide on them, to smooth their surfaces, and to establish some sort of temperature equilibrium.

Much successful analysis is being done with such simple a-c spark sources,[8] although it is usually found necessary to average two or more exposures to improve the accuracy. Klinger, Schliessman, and Zänker[9] announced that it was impossible to perform accurate analysis of steels with the condensed spark. Perhaps enough attention was not paid to the size, form, and spacing of the electrodes, since from some observations which we have made on cast-iron analysis, with a simple spark, it appears that Si may be determined with an error of about ± 6 or 8 per cent of the amount present in a single observation.

As has been pointed out above, it is highly desirable, in spark analysis, that the energy in the condenser at the initiation of each spark train should be the same. One method for approximating this condition, taken over from radio spark transmitters by Feussner,[10] is to place in series in the spark circuit a rotating gap or interrupter, which is timed so that sparking takes place only during a few degrees of motion of the gap and thus always at the same phase and voltage of the condenser cycle. Feussner attacked the problem of uniform decrement by attempting to produce as high a decrement as possible. This he did with an air blast on the gap, a quenched gap in series with the rotating and sample gaps, and an inductively coupled, tuned, quenching circuit. Spark outfits embodying all these features, as well as simpler outfits without the quenching or energy-dissipating features, have

been put on the market by Carl Zeiss, and are reported to permit the spectrographic analysis of metals with excellent accuracy.[11]

They require, however, 3 to 8 minutes pre-sparking — the longer time for the simpler outfit — before uniform results are obtained. It is the small amount of power used, 1 kw at 8000 volts, that necessitates the long pre-sparking time to condition the electrodes. This is a severe handicap when high speed is required, as for control analysis.

We have made an extensive study of spark circuits in our work on high-speed spectrographic analysis. The rotating gap appears to offer some improvement in the reliability of the results obtained. With 10 kw at 40,000 volts, no warm-up time is required, or, at most, 15 seconds is sufficient for uniform results, while an air blast on the gap and a series resistance in the spark circuit control the damping adequately. Results obtained with this outfit were shown at this conference last year.[12]

In the preceding discussion, consideration has been given chiefly to the question of doing analysis on samples which differ significantly only in the concentration of the element under analysis, as in a routine production control. It is often necessary, however, to provide a method of analysis when an element must be determined in the presence of varying amounts of one or more other elements. But varying amounts of foreign materials may affect the temperature of the discharge, by altering the heat conductivity, heat content, or rate of radiation of the discharge. They may also affect the potential gradient in the column by their different ionizing potentials and different transport rates. And, finally, by their different masses and boiling points, they may affect the rate at

which elements are released by the electrodes. All these effects interfere, of course, with accurate analysis, and some method of correction is required. However, if the material is in liquid or powder form which is dried on or packed in a graphite electrode, it is possible to minimize the difficulty by adding to the sample a spectrographic buffer[13] in large enough quantities to control the discharge conditions.

Finally, it should be pointed out that, since in the use of the internal standard method of analysis the results are based on comparison of the relative intensities of a line of the unknown and of a line of the reference element, the effects of all variations in the source would be eliminated by the choice of two lines for comparison which respond in the same way to all fluctuations. Strictly, this would involve the use of an internal standard element with the same disengaging properties (mass and vapor-tension curves) and the same transport properties in the arc, and the use of a spectral line of this element with the same excitation function (transition probability and wave number). It is not possible to satisfy all these conditions, but it is usually possible to choose an internal standard element of nearly the same mass and ionization potential, and to select from the lines of this element a line which behaves in approximately the same way as the chosen line of the element to be determined.

We may conclude by remarking that the best light source for spectrographic analysis is the one, within the limits of permissible external conditions, which behaves in the most uniform and repeatable manner. Variations may be minimized by the use of a suitable buffer element and their effects made innocuous by the selection of a suitable reference line of an appropriate internal standard element.

REFERENCES

1. *Physica*, **2**, 652 (1935).
2. *Physica*, **2**, 45 (1935).
3. RICHARDSON, *Proc. Fifth Conference on Spectroscopy, 1937*, p. 64 (1938).
4. HASLER, *ibid.*, p. 43.
5. *J. Applied Phys.*, **8**, 163 (1927).
6. *Proc. Am. Soc. Testing Materials*, **36**, II, 310 (1936).
7. *Can. J. Research*, **16**, 17 (1938).
8. OWENS, *Proc. Fifth Conference on Spectroscopy, 1937*, p. 17 (1938); GUION, *ibid.*, p. 11.
9. *Arch. Eisenhüttenw.*, **6**, 487 (1933).
10. *Ibid.*, **6**, 551 (1933).
11. KAISER, *Metallwirtschaft*, **13**, 301 (1937); SCHLIESSMAN and ZÄNKER, *Arch. Eisenhüttenw.*, **10**, 383 (1937).
12. *Proc. Fifth Conference on Spectroscopy, 1937*, p. 1 (1938).
13. LANGSTROTH and McRAE, *Can. J. Research*, **16**, 61 (1938).

INFLUENCE OF IMPURITIES ON LINE STRENGTH IN QUANTITATIVE ANALYSIS

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A brief review of some of the literature on the subject of the influence of impurities on line intensities shows considerable divergence of opinion with regard to the magnitude of this effect. It is generally known in emission spectroscopy that under suitable conditions one element may markedly affect the intensity of spectrum lines of another element in a mixture of the two, the classical example being the effect of mercury on the neon spectrum: the addition of a trace of mercury in a neon tube will cause a nearly complete elimination from the usual spectrum of the neon lines, since the electrical energy is almost entirely transferred by the mercury vapor.

With many substances, however, there does not appear to be any marked effect on the line intensities as a result of impurity addition; for example, Gerlach and Schweitzer[1] have shown that potassium chloride could be added to a one to one zinc chloride-cadmium chloride solution until the solution contained 32 per cent of potassium chloride with no perceptible change in the intensity ratio of the zinc and cadmium lines. D. M. Smith[2] has also pointed out that it may generally be assumed that the presence of other im-

purities than the one under investigation has no effect upon the intensity of the lines due to that particular element. This assumption seems justified for small quantities (less than 1 per cent).

Zinc-cadmium alloys which were carefully analyzed and shown to contain a variety of other elements gave satisfactory correlation in relative line intensities as compared with the standard alloys prepared especially for control and known to be free from these impurity elements. The same results were obtained from zinc-iron alloys in which cadmium and lead were present in varying quantities, yet this variance did not appear to affect the systematic increase in intensity of the iron lines with an increase of the iron content. From these and other data, Smith concludes that it may generally be assumed "that the presence of other constituents than the one under consideration has no effect on the intensity of the lines due to that constituent."

On the other hand, T. Negresco[3] states that, in a given alloy, the introduction of a third metal totally changes the sensitivity of the spectrum lines of the other two elements, and cites as an example a copper alloy containing 10 per cent of manganese and 0.1 per cent of aluminum. In the observed spectrum the aluminum lines were practically suppressed. In this alloy,

however, the manganese occurs in a comparatively large quantity, and thus apparently has a more pronounced effect than if it were present only as an additional impurity, i.e., 1 per cent or less. The effect on cadmium lines in a zinc alloy when varying amounts of lead and iron are added is similar.

Van Someren[4] has reported a similar effect with 10 per cent of silicon in an aluminum alloy and 10 per cent of zinc also in an aluminum alloy, both causing a lower intensity in the impurity lines and hence a lower spectrographic analysis figure as compared with the chemical analysis. As a reversal of this effect it may be pointed out that it has been reported that a small amount of material, such as 0.5 per cent tin or arsenic in copper causes a marked increase in the density of the copper lines.

Duffendack, Wolfe, and Smith,[5] in comparing the intensity of barium lines in nickel and nickel copper alloys, noted that there was an appreciable effect of copper on the relative intensities of the Ba lines. These examples thus confirm the general principle that for each substance to be analyzed due consideration must be given to the effects of each substance present on the line intensities of all the other substances present. For accurate analyses this would involve the preparation of standard or working curves with as nearly as possible the same content as the unknown, and where more than one unknown is present in variable amounts the working curve experimentation should include a study of the effect of the variation of each of the possible constituents on all the other constituent line intensities.

Such a series of experiments was carried out by Twyman and Hitchen[6] in which they studied the influence of iron and copper on the intensities of nickel and cobalt, using chromium as the internal standard

(Fig. 1). From these data they concluded that, although many complex factors may take part in the influence of one element on the line intensities of another, the effect is not so great but that a direct examination of the unknown substance will give the concentration of the constituents to a first approximation. A series of known standards can then be prepared and the influence of the variation of the constituents present on the line intensities of one another can easily be determined. This
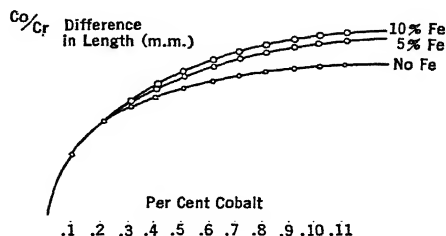
FIG. 1. Influence of Iron on the Working Curve for Cobalt Line Pair Co 3405.12/Cr 3403.32.
(Twyman and Hitchen)

correction can then be applied to the original unknown analysis, or if a series of samples are to be run a working curve may be set up for the particular type of material under observation.

Duffendack, Wiley, and Owens[7] have further investigated this effect of one element on intensities of another, and they divide these variations into two types, those dependent on solution characteristics and those dependent on elemental interactions in the vapor state in the arc or spark. Sodium, potassium, and magnesium were found to decrease certain elements when compared with cadmium, and calcium enhanced the intensities of the potassium and magnesium with respect to cadmium.

Negative ions are known to have some effect on line intensities, and it is reported that the chloride ion will increase the in-

tensities of lines without changing the relative intensities, whereas sulfate and phosphate ions are reported to cause a decrease in intensities without an appreciable change in relative intensities.

Personal observations by the authors have indicated that in certain cases such as the chlorides of the alkali earth metals, a considerable amount of the element is excited as the calcium, strontium, or barium subhalide to give the corresponding diatomic band spectra. In fact, a method for the determination of fluorides has been reported in which the salt is mixed with $CaCO_3$ and arced and the intensity of the CaF band spectra used to determine the amount of fluoride present. Certainly a portion of the alkali earth metals, at least in low-temperature arcs, is excited in the form of the oxide rather than the elemental state, and this would apply to the sulfate and phosphate salts which would yield oxides at the arc temperatures.

A rather important observation was made by Duffendack, Owens, et al., namely, that the influence of the extraneous element on the line intensity of the impurity, as compared with an internal standard, reached a maximum value, and by use of what might be termed a method of excess, i.e., addition of an excess of this extraneous element, it was possible to eliminate the necessary consideration of the effect of the extraneous element on the unknown. The use of an excess-method some times reduces the sensitivity of the unknown lines to slight changes in percentage composition. This is especially true of the addition of potassium in excess to an unknown containing calcium. Other workers in the field of spectroscopy have suggested the possibility of establishing an ordered arrangement of elements much as in an electromotive series, in which the order follows the ionization potentials with the indication that any element might have its lines depressed or enhanced by elements above or below it in the series. There appear to be numerous exceptions to this order, however, and further work seems to be necessary in this field.

TABLE I

COMPOSITION OF SAMPLES
(Breckpot, Creffier, and Perlinghi[8])

No.	Grams of		
	Lead	Antimony	Tin
1	99.7	0.3	0.3
2	99.7	0.3	1.0
3	99.7	0.3	3.1
4	99.0	1.0	0.3
5	99.0	1.0	1.0
6	99.0	1.0	3.1
7	97.0	3.0	0.3
8	97.0	3.0	1.0
9	97.0	3.0	3.1

Breckpot, Creffier, and Perlinghi[8] have recently shown that the addition of quantities smaller than 0.3 per cent of an extraneous element to a binary system had little or no effect on the relative intensities of the binary components and in some instances as much as 3 per cent could be added before any measurable effect could be noted. For example, they studied the lead-antimony alloys with 0.3, 1.0, and 3.0 per cent antimony, to which were added known amounts of tin as indicated in Table I and Fig. 2. They found the effect of tin on the lead-antimony intensities to be nil when the amount of antimony was 0.3 per cent, but when it was increased to 1.0 and especially when increased to 3.0 per cent there was a marked effect of variation of tin on the antimony lines, a dis-

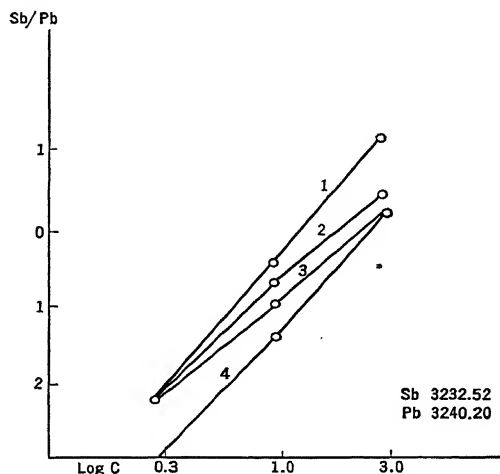tinct depression of the intensity of the antimony lines accompanying an increase in the amount of tin present. Antimony, on the other hand, appears to be more affected by lower amounts of tin* than higher amounts, the effect reaching a maximum around 0.3 per cent and disappearing at concentrations below 0.1 per cent.

To supply further information to this problem of influence of line intensities we have prepared a series of samples of cadmium and zinc, using in our analyses the homologous pairs of 3252.5 (Cd) and 3345.0 (Zn). The mixtures used were made up in an alumina-silica base of constant composition,[9] and to avoid chemical reaction the salts used were either as carbonates or sulfates but not mixtures of carbonates and sulfates. In the samples studied a mixture of 4 parts of cadmium as carbonate with 1 part of zinc as carbonate was mixed with 10 per cent of this amount of each of the following metals as carbonates; sodium, potassium, lead, magnesium, copper, and bismuth. It was found that only the last two in this concentration had an appreciable effect on the relative intensity of the Cd-Zn lines, and their effects were in opposite directions. The presence of copper reduced the in-

Fig. 2. Influence of Tin on the Working Curve for Antimony

1. Pb–Sb system   0.3 % Sn
2. Pb–Sb system   1.0 % Sn
3. Pb–Sb system   3.0 % Sn
4. Arc Metal without Sn

(Breckpot, Creffier and Perlinghi)

TABLE II

EFFECT OF VARIOUS AMOUNTS OF COPPER AS THE CARBONATE ON THE CD–ZN LINE RATIO

Alloy			Line Intensity		Difference
			Cd (3252.5)	Zn (3345.0)	
1.	Cd–Zn mixture		8.1	9.5	1.4
2.	" " "	10% Cu	8.1	8.8	0.7
3.	" " "	5% Cu	8.5	9.2	0.7
4.	" " "	2.5% Cu	7.6	9.0	1.4
5.	" " "	1.25% Cu	8.0	9.6	1.6
6.	" " "	0.625% Cu	7.7	9.4	1.7
7.	" " "	0.312% Cu	7.5	9.0	1.5
8.	" " "	0.156% Cu	7.0	8.6	1.6

TABLE III

EFFECT OF VARIOUS AMOUNTS OF BISMUTH AS THE CARBONATE ON THE CD–ZN LINE RATIO

Alloy			Line Intensity		Difference
			Cd (3252.5)	Zn (3345.0)	
1.	Cd–Zn mixture		9.0	10.4	1.4
2.	" " "	10% Bi	6.0	8.5	2.5
3.	" " "	5% Bi	4.7	7.0	2.3
4.	" " "	2.5% Bi	6.9	8.4	1.5
5.	" " "	1.25% Bi	5.5	7.0	1.5
6.	" " "	0.625% Bi	7.2	8.6	1.4
7.	" " "	0.312% Bi	5.7	7.2	1.5

tensity of the Zn lines compared with the Cd line (Fig. 3). Bismuth, on the other hand, reduced the intensity of the Cd line
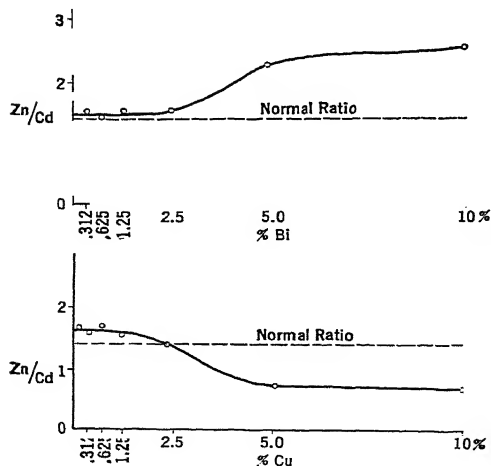
FIG. 3. Upper. Influence of Bi on the Zn-Cd Line Ratio (Carbonates). Lower. Influence of Cu on the Zn-Cd Line Ratio (Carbonates).

compared with the Zn lines. The spectrogram of copper and bismuth carbonates showed no lines at 3252.5 A and 3345.0 A,

which would of course make any comparison impossible.

The same series of experiments was repeated using the sulfates rather than the carbonates. The results as indicated in
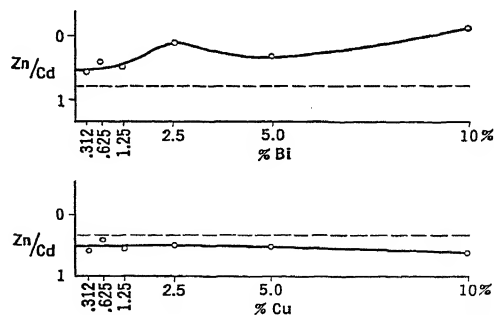
FIG. 4. Upper. Influence of Bi on Zn-Cd Line Ratio (Sulfates). Lower. Influence of Cu on Zn-Cd Line Ratio (Sulfates).

Fig. 4 show that the effects, though not as great as with the carbonates, are in the same direction, with an increase in the zinc as compared with the cadmium on the increase of the amount of bismuth and a decrease in the intensity ratio on the increase in the amount of copper added.

Like other workers in this field, we have noted that the effect produced is slightly below about 2 per cent of extraneous metal and in the series studied the effect becomes fairly constant above a concentration of about 5 per cent of extraneous metal. The same type of effects has been noted in studies which we have made in this laboratory on the effect of large amounts of iron on the suppression of the sensitivity of the boron lines.

Conclusion. From this study of extraneous element influence on the relative intensity of line pairs it would appear that the effect is limited to certain concentration ranges and that on either side of the sensitive region the effect can be considered as constant in character. It has also been shown that the effect may be positive as well as negative with regard to the influence on line intensity. For complete quantitative analyses it is recommended that working curves be prepared in which the extraneous elements are in equivalent quantity to that of the unknown series, and where some doubt exists as to their effect a set of working curves should be prepared with different concentrations of the extraneous elements.

REFERENCES

1. GERLACH and SCHWEITZER, "Foundations and Methods of Chemical Analysis by the Emission Spectrum."
2. D. M. SMITH, *Trans. Faraday Soc.,* 26, 101 (1930); *J. Inst. Metals,* 46, 114 (1931).
3. NEGRESCO, "Recherches expérimentales d'analyse spectral quantitative sur les alliages métalliques," p. 46 (1927).
4. VAN SOMEREN, *J. Inst. Metals,* 55, 273 (1934).
5. DUFFENDACK, WOLFE, and SMITH, *Ind. Eng. Chem.,* Anal. Ed., 5, 226 (1933).
6. TWYMAN and HITCHEN, *Proc. Roy. Soc. (London),* A. 133, 72 (1931).
7. DUFFENDACK, WILEY, and OWENS, *Ind. Eng. Chem.,* Anal. Ed., 7, 40 (1935).
8. BRECKPOT, CREFFIER, and PERLINGHI, *Ann. Soc. Sci. Bruxelles,* Ser. I, 57, 295 (1937).
9. BRODE, *Proc. Fifth Conference on Spectroscopy, 1937,* p. 60 (1938).

THE QUANTITATIVE SPECTROCHEMICAL ANALYSIS
OF
MIXTURES OF GASES

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The quantitative spectrochemical analysis of solid materials and of solutions and other liquids has been developed to a very satisfactory degree of accuracy. The many advantages of these methods have caused a rapid spread in their use in various industries. The ability to measure accurately minute traces of impurities in materials by spectroscopic means, to make analyses of small samples, and to attain high speed without loss of accuracy are particular advantages of these methods that have contributed largely to their wide adoption. The quantitative analysis of mixtures of gases by spectroscopic methods, however, has not been developed to a satisfactory degree. Some difficulties have been encountered which have thus far held back the use of the spectrograph in this field though the same advantages would make it extremely valuable. In this paper we will discuss some of the difficulties that have been encountered and means for overcoming them.

Very little has been published on the spectroscopic analysis of gases though undoubtedly much work has been done. One of the researches published which illustrates the difficulties commonly encountered is the determination of hydrogen and of helium in mixtures of these two gases.[1] The relative intensities of spectral lines of the constituent gases may vary with the total pressure of the gas in the discharge tube even though the relative amounts of the constituents remain constant. This difficulty can easily be avoided by always introducing into the discharge tube the same amount of gas. However, nearly all gases disappear from discharge tubes during the passage of the discharge because of the operation of one or more of the agents causing clean-up. The rate of clean-up is different for different gases, and so the proportions of the several constituents of a mixture of gases will not remain constant when an electric discharge is maintained in the tube. As a consequence the relative intensities of the spectral lines of the constituents will not remain constant, and so the use of an internal control fails except over a narrow range of amounts present. It has been found possible, however, to use the helium lines for internal control in the determination of small amounts of nitrogen or of carbon monoxide in a large excess of helium.

The rate of clean-up of gases varies markedly with the type of discharge and with the voltage applied to the electrodes. Hot-filament tubes cannot be employed

with some gases for this reason, and high voltages must also be avoided with some. Therefore the types of electric discharges that can be used are somewhat limited, but most gases can be satisfactorily excited in one or another region of the glow discharge or by means of some type of electrodeless discharge. In the experiments to be described, the positive column of a glow discharge proved satisfactory.

Besides difficulties due to clean-up, variations in the intensities of the lines of certain elements resulting from changes in the amount of another gas present are frequently encountered. These so-called interferences of atoms of one kind with the analysis of elements of another kind are particularly troublesome in many mixtures of gases, especially when helium or another of the rare gases is present. Therefore it becomes necessary to determine whether such effects are present and to take measures to avoid or minimize them.

The solution to a number of these problems came as a result of two measures which were adopted, namely (1) the use of helium in excess as the carrier of the electric discharge, and (2) the use of a small addition of argon as the internal control.

The choice of helium as the carrier was made because of several properties of this gas. In the first place, its rate of clean-up is negligible when cathodic sputtering is avoided and so the pressure of the gas in the discharge tube will remain constant over a considerable period of operation. Then too the excitation and ionization potentials of helium are higher than those of any other gas and so helium does not limit the velocities of the electrons to values too low to excite other molecules that may be present. It is true that metastable helium atoms often make collisions of the second kind with molecules

of other gases, but these effects are taken into account in the working curve and cause no difficulties. In fact, such impacts sometimes are advantageous as they probably make it possible to detect extremely minute traces of hydrogen, nitrogen, and carbon monoxide in helium. Another reason for using helium as the carrier gas is that it can be rather easily purified to a very high degree previous to its use for analytical purposes, and this can be accomplished without any loss of gas. The helium spectrum contains relatively
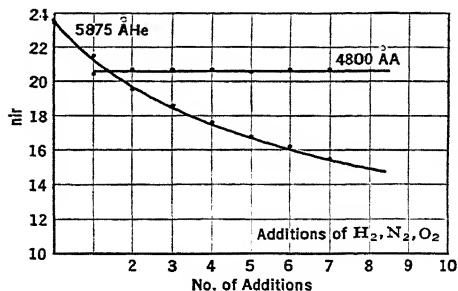
FIG. 1

few lines, and so the chance of the coincidence of its lines with those of the test elements is not great even when a spectrograph of small dispersion is used.

Helium makes an ideal carrier gas, but it cannot be used at the same time as an internal control except in a few instances and then only over rather narrow ranges of pressure. As may be seen from Fig. 1, the intensities of the helium lines are affected by changes in the amounts of other gases present. Hydrogen and oxygen, especially, cause a marked decrease in the intensities of the helium lines, consequently the relative intensities of the lines of other elements with respect to those of helium will vary with the amount of other gases present at the same time. The use of a constant lamp as an external control makes

it possible to avoid the difficulty resulting from interference in some cases, as the writers point out in another paper (p. 97), but it is possible to employ an internal control as will now be described.

When a small amount of argon was introduced into the helium, it was found that the intensities of the argon lines remained remarkably constant even when considerable amounts of other gases were added to the mixture. Fig. 1 gives the results of tests made upon the constancy of the argon lines. Exposures of the same duration were made upon a photographic plate from time to time from the positive column of a glow discharge in a mixture of helium and various other gases. The discharge was always operated at the same voltage and current, and after the plate was developed the densities of certain helium and argon lines were measured with a microphotometer. It will be noted that the density of the argon line remained remarkably constant even with the addition of hydrogen, nitrogen, oxygen, and carbon monoxide each to a pressure of 0.25 mm to helium at a pressure of 2 mm. The intensity of the helium line did not remain constant. In fact, the intensity of the argon line remained the same after the helium line had completely disappeared from the spectrum and bands due to some of the admixed gases had become very intense. The maximum deviation of the density of the argon line from the mean was only 1.5 per cent, which is within the variation one may expect in the photographic emulsion. Thus argon serves as an excellent internal control in these analyses. Furthermore, the spectrum of argon is so strongly excited in a mixture with helium that only a minute amount of argon need be added as only a few argon lines are necessary for analytical purposes.

The discharge tube used for the analyses was a simple glow discharge tube with a quartz capillary 3 mm in diameter. The electrodes were hollow nickel cylinders 15 mm in diameter and 3 cm long, and were mounted on tungsten lead-in wires sealed into Pyrex bulbs. The electrode bulbs were sealed to the quartz capillary by means of graded seals. An a-c glow discharge was excited in the gas mixtures by means of a neon-sign-type transformer rated at 12,500 volts in the secondary on open circuit when the primary was excited by means of a 60-cycle 110-volt supply. The current through the discharge tube was maintained at 25 ma. Care was taken to exclude mercury vapor from the tube at all times. The electrodes were degassed and the helium was purified by well-known methods.

Experiments were made with helium at pressures from 0.5 to 8.0 mm. The higher pressures of helium were advantageous because they permitted a longer range of pressures of the test gases for the analyses. A pressure of helium less than 2 mm is not recommended. The pressure of the argon added to the helium was varied from 0.001 to 0.08 mm. In most of the work a pressure of 0.01 mm was found to be satisfactory. The lower pressures are, in general, desirable as only a few argon lines are needed and argon can be detected in helium to one part in ten million. A pressure of 0.08 mm of argon in 2 mm of helium was found to be too much as at this pressure the intensities of the argon lines were found to vary with the amount of some of the test gases present.

The gases whose amounts have been determined by these methods thus far are hydrogen, oxygen, nitrogen, and carbon monoxide. As carbon dioxide is dissociated in the glow discharge and produces the bands of carbon monoxide, it may be added to the lists of test gases. When car-

bon dioxide is present it must be separated from the carbon monoxide and the proportion of each determined by some other means as by condensing the carbon dioxide in a tube cooled by liquid air. These gases were chosen for the experiments because it is so frequently desired to determine the amounts of them present in the gases resulting from industrial operations. Thus far analytical working curves have been determined for these gases over the following pressure ranges:

Hydrogen 0.0001 to 0.0075 mm.
Nitrogen 0.004 to 0.25 mm.
Oxygen 0.02 to 0.12 mm.
Carbon monoxide 0.001 to 0.10 mm.

When the logarithm of the amount of the test element is plotted against the logarithm of the relative intensities of the selected line of the test element and one of
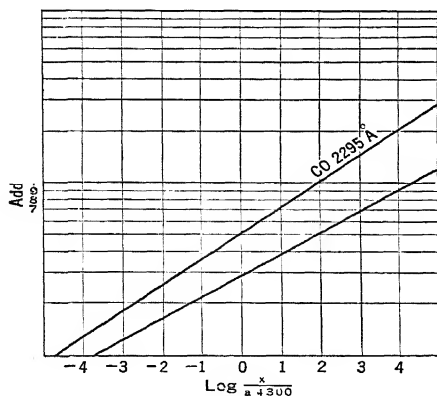
FIG. 2. The lower line is H 4861.

the argon lines, the analytical curves are straight lines over the pressure ranges given above. These ranges were for helium at a pressure of 2 mm. At higher pressures of helium, it may be possible to extend the ranges. However, in the analysis of gases it is always easy to adjust the amount of the unknown introduced into the discharge

tube until the pressures of the test gases come within any chosen range.

With carbon monoxide and nitrogen the edge of one of the bands was used for the
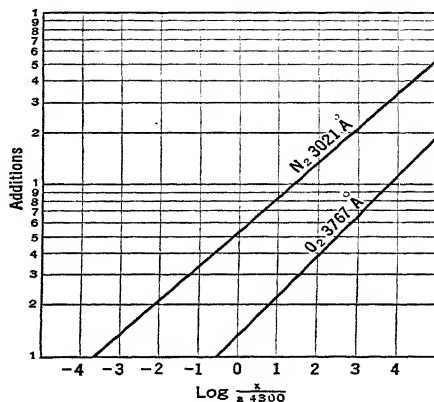
FIG. 3

comparison of intensities as line spectra come only from atoms. The use of band edges did not introduce difficulties, and the precision of the measurements seems to be as good as when lines are used. With the other gases, sufficient dissociation was produced by the electric discharge so that lines due to their atoms appeared in the spectra and were used for the analyses. The lines used for the analytical curves shown in Figs. 2 and 3 are as follows: hydrogen, 4861; nitrogen, band 3021; oxygen, 3967, and carbon monoxide, the band edge at 2295.2 A. These were all compared with the argon line at 4300.1 A. For oxygen it may be found that the use of the red line at 7772 A would enable one to extend the range of analysis to lower percentages.

The analytical procedure pursued was as follows: Into a thoroughly outgassed glow discharge tube a mixture of argon and helium in the proportion previously found to be satisfactory was introduced very

slowly through a liquid air trap to a pressure of 2 mm. This gas mixture was examined for purity by means of a spectroscope or by photographing the spectrum of the glow. One can usually tell from the color of the glow if any considerable amount of impurity is present. If the gas was not absolutely pure, a glow discharge was maintained in the tube until the gas became pure. A measured amount of the unknown specimen was then introduced into the tube. This can be done easily in a manner that can be exactly repeated by first collecting some of the gas in a small bulb or section of a capillary tube and regulating the pressure in this bulb by means of a mercury lift to a fixed value. Thus a definite amount of the unknown gas can be collected, and this gas then can be introduced into the discharge tube. The amount of the unknown that must be added to the discharge tube in order to bring the amounts of the test elements within the analytical ranges may have to be determined by a preliminary experiment. By adding small increments of the unknown and photographing the spectrum of the glow after each addition, one can often find suitable spectrograms for making the determinations of the amounts of each of the test gases without previous trial. The rest of the procedure is identical with that followed in the analysis of solids or of liquids.

Test runs were made to show that the working conditions were reproducible. A limited number of runs were also made using a wide variation in the percentages of the test gases. These tests were also satisfactory. From these results it seems that the method can be applied when small amounts of one gas are present with large amounts of other gases. Further testing is necessary to determine the effect, on the working curves shown, of having other types of gases also present.

However, each application of the method leads to different working conditions, and it will be necessary to check carefully all factors involved before making up exact working curves. This requires a large amount of time and was outside the boundaries of this investigation.

REFERENCE

1. F. KLAUER, *Ann. Physik,* Fünfte Folge, 20, 145–160 (1934).

CHARACTERISTICS OF THE EAGLE MOUNTING OF THE CONCAVE GRATING

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The ideas of spectroscopists on what should be considered the best mounting for a concave grating have undergone considerable change since Rowland's time. The original Rowland mounting, which was universally used at first, is disappearing more and more, and a number of other mountings have replaced it. The question arises which of the various mountings possesses the greatest advantages, so that it can be recommended as the most useful.

There is no definite answer to this question. No single mounting combines all the advantages, and therefore one who is about to acquire a grating spectrograph must ask himself first for what purpose that spectrograph is chiefly intended and what his resources and facilities are, and then make his choice.

In many cases the Eagle mounting will be the most useful, and, although it has been used widely, it has not acquired quite the popularity it deserves. The reason for this is probably that too much weight is attached to a few minor inconveniences. In the present article I should like to show that a properly constructed Eagle mounting may very well be considered the universal mounting and, in my opinion, should be the choice of small institutions, industrial organization, etc., for which it is impossible to have more than one spectrograph. In most cases it can, with advantage, replace big prism spectrographs. It will be shown that the astigmatism which is usually considered a serious drawback for many applications can be removed easily and effectively.

In order to realize the advantages and disadvantages of the Eagle mounting, it is advisable to consider briefly the various mountings now in use, and compare their properties.

COMPARISON OF THE DIFFERENT GRATING MOUNTINGS

1. **Rowland Mounting.** Slit fixed. Plate holder and grating movable in such a way that the spectrum always is photographed in the normal. This property was considered a great advantage when the accurate determination of wavelengths was the chief purpose of the grating spectrograph, as the dispersion is very nearly constant over the whole plate. However, since it was found that the interferometer is a much more reliable instrument for accurate wavelength measurements than the concave grating, the normality of the spectrum is of much less importance.

The disadvantages of the Rowland mounting far outnumbered its one advantage. Its construction and adjustment

are fairly complicated. It has movable parts and cannot be kept adjusted permanently. Finally, its astigmatism is very large compared to that of the other mountings.[1] Similar arguments apply to the Abney mounting which, though its adjustment is somewhat simpler than that of the Rowland mounting, has the additional disadvantage that the slit is not fixed and therefore the light source must be moved in going to different spectral regions.

2. Paschen Mounting. With this mounting there are no movable parts. Grating and slit are firmly mounted on concrete piers in their proper places on the Rowland circle. The plate holder is also fixed and can, if desired, extend practically along the whole Rowland circle, so that all wavelength regions and all orders can be photographed simultaneously.

The obvious advantages of this mounting have made it probably the most popular one. As there are no movable parts, the rigidity is very great, if it is mounted on a stable foundation. No further focusing is necessary after the initial adjustments are made, and the spectrograph is always ready for use for all regions of the spectrum.

The astigmatism may be considerable. It depends on the angle which the incoming rays form with the normal of the grating. It can be kept to a minimum by employing several slits under different angles of incidence, although some of the advantages of this mounting are then lost.

The one great disadvantage of the Paschen mounting is its need for space. Hardly any laboratory contains rooms suitable for housing a big Paschen mounting except those designed for this purpose before the laboratory was built. This requirement for much space and the difficulty of a satisfactory temperature control are the biggest handicap for the

Paschen mounting and make its use impracticable in many institutions.

3. The Wadsworth Mounting. If parallel light falls on a grating, the spectrum produced near its normal will be completely free from astigmatism. This was first demonstrated by Wadsworth,[2] and therefore a mounting using a concave grating in parallel light is now commonly called a Wadsworth mounting, although some of its features were developed by other observers. It was shown by Zernike[3] that the second-order image errors are also absent at the normal, so that this mounting is to be considered a very excellent one. A detailed description of a mounting of this type used at the Bureau of Standards was given by Meggers and Burns.[4]

Anyone for whom freedom from astigmatism is the chief consideration will do well to consider this mounting. The plate is closer to the grating than with the other mountings, which reduces the dispersion to about half. This must in general be considered a disadvantage, as, with most photographic plates, the full resolving power of a big grating cannot be utilized On the other hand, the relative aperture is increased so that the spectrograph is faster than the same grating used in a different mounting.*

The disadvantage of this mounting is that it is relatively expensive. The best way to render the rays coming from the slit parallel is by a concave mirror which must be of the same optical quality as the grating itself.

In order to reach the different spectral

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*This is the usual statement made in the literature. Properly the Wadsworth mounting should be compared with another mounting of a grating of about half the focal length which has the same dispersion. Then there will be no increase in intensity, except that due to the absence of astigmatism, and there will be the loss due to the additional reflection on the collimating mirror.

regions it is necessary to turn the grating and move the plate holder. The focal curve is not a circle, but a parabola, and the motion of the parts is more complicated than in the Eagle mounting and the construction has accordingly to be carried out with more care.

Finally the space occupied by the Wadsworth mounting is considerably larger than that of an Eagle mounting of equal dispersion, though smaller than that of a Paschen mounting. It is about the same as that needed for a Rowland mounting.*

4. The Eagle Mounting. In this mounting the plate holder is near the slit, so that the angle of incidence is always very nearly equal to the angle of emergence. This gives the Eagle mounting a compactness not equaled by any other mounting of the concave grating. The fact that it occupies little space makes thermostating relatively easy and reliable. The astigmatism, at least for the lower orders, is near the minimum value it can have under any circumstances for these wavelengths.

However, changing over from one region of the spectrum to another means moving both grating and plate holder. This need be no very serious disadvantage with any properly constructed spectrograph, as the movement is quite simple. The region of the spectrum which can be photographed simultaneously is limited by the length of the plate holder. This is determined by considerations of convenience of handling. It is 16 inches for our 15-foot spectrograph, which means that it covers about 1500 A. It can be made twice as large if desired. Only then the compactness of the spectrograph and the

ease with which adjustments can be made would suffer, but the lines would be uniformly sharp over its total length, as the plates are made to coincide everywhere with the Rowland circle.

If we compare the mountings discussed above, we find that, for present-day needs, the disadvantages of the Rowland and Abney mountings outweigh their advantages, but that the Paschen, Wadsworth, and Eagle mountings each have features which render them very useful, and a laboratory which intends to specialize in spectroscopic research should not restrict itself to one type of mounting, but have two or preferably all three.

The question is now what a laboratory should do which can afford only one spectrograph, or an industrial laboratory where ease of handling and compactness are often the chief requirements.

For such a laboratory there is no doubt in my mind that the Eagle mounting is the most useful one, and its advantage is even enhanced if the price at which the different spectrographs can be built is taken into consideration. I would even go as far as to maintain that in most institutions where a big prism spectrograph is used it can be replaced with advantage by an Eagle mounting of a concave grating.

The Eagle mounting can be built easily and quite cheaply in any laboratory workshop, and use can be made of a discarded lathe bed for a rigid support of the grating. The lead screw of the lathe can be used to move the grating back and forth. I shall omit here all details of construction, as a precision mounting of this type is described in the article by W. S. Baird in this volume.

Owing to its great compactness the Eagle mounting can be very easily and effectively thermostated. Uniform temperature is ab-

*The considerations of space are, of course, the more important the larger the focal length of the spectrograph. For small spectrographs they are entirely immaterial.

solutely essential if long exposures are required.

At first sight the Eagle mounting together with all the other mountings of the concave grating seems to be inferior to the Wadsworth mounting as far as the astigmatism is concerned. As the astigmatism is usually a very serious drawback, I want to devote the rest of this article to it and show that it can be removed quite easily and effectively in the Eagle mounting with the help of cylindrical lenses. It is best, however, to treat the question of astigmatism in general rather than restrict ourselves to the Eagle mounting in particular.

THE ASTIGMATISM OF THE CONCAVE GRATING AND SOME METHODS FOR CORRECTING IT

A point on the slit of a concave grating spectrograph will have as its image on the Rowland circle, not a point, but a vertical line. This property, called astigmatism, is found whenever lenses or mirrors are used off their optical axis. The magnitude of the astigmatism is given by the length of the focal line into which the point is drawn out. This length is proportional to the length of the rulings and therefore depends on the individual grating used. A more universal quantity is the astigmatism ζ per unit length of ruling. It is a function of the geometrical arrangement of the spectrograph only.

The astigmatism must be considered a serious disadvantage for most purposes. It is an inherent property of all mountings of the concave grating except the Wadsworth mounting. If we are interested chiefly in photographing the lines of a spectrum and measuring them, the only harm the astigmatism does is to reduce the intensity. If, however, we want to use a diaphragm on the slit either for a comparison spectrum or as a step reducer for intensity measure-

ments, we need a stigmatic image of the slit and the astigmatism will make the use of such devices entirely impossible. A strictly stigmatic image is also required when an interferometer is used with the spectrograph.

We shall discuss the influence of the astigmatism on the intensity first. If only a short portion of the slit is illuminated, the intensity of the spectral line is reduced because the image is drawn out into a vertical direction. The intensity can be increased by illuminating a large part of the slit, and it reaches the value which it would have for a stigmatic image if the length of the illuminated slit is equal to the astigmatism divided by the magnification.* A further increase in the length of the illuminated slit would not increase the intensity any more.

A serious loss of intensity can therefore occur only if the astigmatism is considerable or when it is not possible for some reason to illuminate a large enough portion of the slit. It is true that theoretically the effect of any amount of astigmatism on the intensity can be counteracted by illuminating a long enough part of the slit. For a considerable amount of astigmatism, however, that would be impracticable, as the length of most slits is limited. There is also a limit to the size of an image of a capillary tube seen end on, as it is necessary that the cone of light fill the grating completely. In addition a too long slit would seriously affect the resolving power of the grating. Each vertical line into which a point on the slit is drawn out on the Rowland circle is not entirely straight but slightly curved, and a superposition of these curved lines over a long vertical range would blur the line (see Zernike[3]).

*The magnification is not very different from one except in extreme cases.

For all these reasons we can be sure that, as far as the intensity is concerned, a small amount of astigmatism is without any consequence, whereas a larger amount is decidedly harmful. We can, rather arbitrarily, put the limit of astigmatism which can be tolerated in this connection as 1 cm or about $\zeta = 0.2$ if the grooves of the grating are 5 cm long.

If we want to use the grating for intensity measurement or with the interferometer, or in any other way where a stigmatic image is essential, even a small amount of astigmatism cannot be tolerated, and we must remove the astigmatism completely.

How this can be achieved can best be seen from some simple geometrical considerations (Fig. 1).

If the incident light forms the angle α with the normal and the emergent light the angle β, then there are two focal
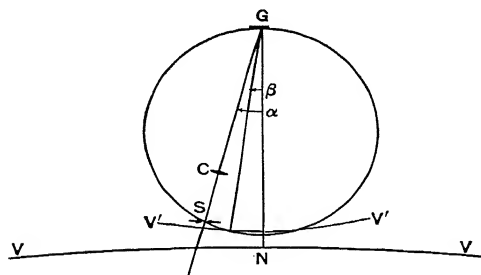
curves. The first, which we call the horizontal focus, is the ordinary Rowland circle. A point on the slit will give a sharp image on this curve in a horizontal plane only, but will be drawn out to a line in a vertical plane. The vertical focus is a different curve V, and on this curve we get a vertical image (a point on the slit will be drawn out on this curve in a horizontal line). The curve for the vertical focus lies

back of the Rowland circle as is indicated in the figure.

We can treat the image formation of the grating with radius of curvature R, now independently in a horizontal plane where we have a focal length F and a vertical plane where the focal length is f. From the knowledge that the horizontal image is on the Rowland circle and that the astigmatism ζ is given by

$$\zeta = \sin^2 \beta + \frac{\sin^2 \alpha \cos \beta}{\cos \alpha} \qquad (1)$$

we find that

$$\frac{1}{F} = \frac{1}{R \cos \beta} + \frac{1}{R \cos \alpha} - \frac{\cos \alpha \cos \beta}{f} \qquad (2)$$

$$\frac{1}{f} = \frac{1 - \zeta}{R \cos \beta} + \frac{1}{R \cos \alpha}$$

$$\frac{\cos \alpha + \cos \beta}{R} = \frac{\cos \alpha \cos \beta}{F} \qquad (3)$$

From this we get as equation of the vertical focal curve (distance from grating v)

$$\frac{R \cos \beta}{1 - \zeta} = \frac{R}{\cos \beta - \dfrac{\sin^2 \alpha}{\cos \alpha}} \qquad (4)$$

A correction of the astigmatism can now be accomplished by inserting somewhere in the optical path a cylindrical lens with a horizontal axis perpendicular to the optical axis of the spectrograph.

In the horizontal plane the lens acts only as a thin plane-parallel plate and has no appreciable effect on the focus. In the vertical plane, however, it acts as a lens, and by a suitable choice of its focal length and position the vertical focus can be shifted in such a way as to make it coincide with the horizontal focus. It is obvious that this cannot happen simultaneously for the whole Rowland circle, but that the astigmatism is canceled completely only for one or possibly two points

on the Rowland circle. But in the vicinity of these points the astigmatism will be small and will not be harmful.

Use of a Cylindrical Lens between Slit and Grating. The problem now is to put a cylindrical lens C between slit and grating so that the astigmatism is removed for a certain region of the spectrum. This problem can be solved without difficulties by treating the system consisting of cylindrical lens and grating as a compound optical system and specifying that the focus fall on the Rowland circle.

The condition for astigmatism is

$$\phi(1 - \cos \alpha \cos \beta) = g^2 (\cos \beta - f) + \\ g (1 - \cos \alpha \cos \beta) \qquad (5)$$

in which

$\phi =$ the focal length of the cylindrical lens.

$g =$ the distance of the cylindrical lens behind the slit.

$f =$ the vertical focal length of the grating for $R = 1$ given by (3).

$\alpha =$ the angle of incidence.

$\beta =$ the angle of emergence.

All linear quantities are given in terms of the radius of curvature R of the grating as unit. (5) is therefore applicable to gratings of any size, and, in order to get the quantities ϕ, g, and f in centimeters, they have to be multiplied by the value of R for the particular grating.

α, β, and the grating space d are connected by the well-known equation

$$\lambda = d (\sin \alpha + \sin \beta) \qquad (5)$$

For the special case of the Eagle mounting ($\alpha = \beta$) the condition for astigmatism becomes

$$(\phi - g) \sin \alpha \tan 2\alpha = g^2 \qquad (6a)$$

For the Rowland mounting ($\beta = 0$) this becomes

$$(\phi - g) \sin \alpha \tan \alpha = g^2 \qquad (6b)$$

From these formulas the order of magnitude of the focal length of the most suitable cylindrical lens can be found. If we want to put the cylindrical lens, e.g., at a quarter the slit-grating distance behind the slit, it must have at least a quarter the linear dimensions of the grating. The vertical dimension should be larger than that if no light is to be lost, as the lens will contract the beam in the vertical direction.

In the following table the focal length for the cylindrical lens which will render the Eagle mounting stigmatic when it is placed in that position is given for different values of α. The second column gives the wavelength for a 15,000-line-per-inch grating, and the last column the focal length of the cylindrical lens in centimeters for a 21-foot grating.

α	λ (in A)	ϕ	ϕ in Centimeters for 21-ft Grating
5°	2,950	4.28	2780
10°	5,880	1.21	783
20°	11,600	0.427	278
30°	16,900	0.271	176
40°	21,800	0.202	131
50°	25,900	0.155	101
60°	29,300	0.115	74.5
70°	31,800	0.076	49.6
80°	33,300	0.038	24.8

If the focal length of the cylindrical lens is smaller than that given in the table, it will have to be closer to the slit. Then the vertical magnification will be increased, and sometimes a too large value of this magnification is not desired.

If, on the other hand, the focal length of the cylindrical lens is longer, it will have to be moved closer to the grating and its size will have to be accordingly larger. For

average use I would suggest a lens of about 250-cm focal length for the first order of the visible and photographic infrared. If the higher orders are wanted, the focal length should be shorter, and all the desired information can be obtained from the table or equation (5).

For a Paschen mounting with an angle of incidence of about 40° we have found a focal length of 150 cm very useful. For the Rowland mounting it should be even shorter. Cylindrical lenses for gratings with a different radius of curvature will have their focal lengths changed in proportion.

Equation (5) can also be used to find the exact position of the cylindrical lens for any wavelength. However, an empirical determination of that position is much more practicable and convenient. For, quite apart from the fact that the solution of (5) for the distance g is laborious, we must besides take into account the variation of the focal length of the cylindrical lens due to the dispersion of the material of the lens.

However, the experimental adjustment of the lens presents not the slightest difficulties if it is properly mounted. In mounting the lens it is absolutely essential that the cylinder axis be exactly horizontal, and small deviations from this position will show considerable deterioration in the definition of the image. Therefore the lens is mounted on a tube which can slide smoothly in another tube which is fixed on a stand. The adjustment of the movable tube with respect to the fixed tube can be very minutely regulated by screws (Fig. 2). The best way to adjust the orientation of the cylindrical lens is to watch the sharpness of a line while an assistant turns the adjusting screws. The best orientation is obtained when the definition of the line is best. The lens holder is

mounted on an optical bench so that it can be moved in the direction of the optical axis.

By moving the lens back and forth, the position is easily found which will give a
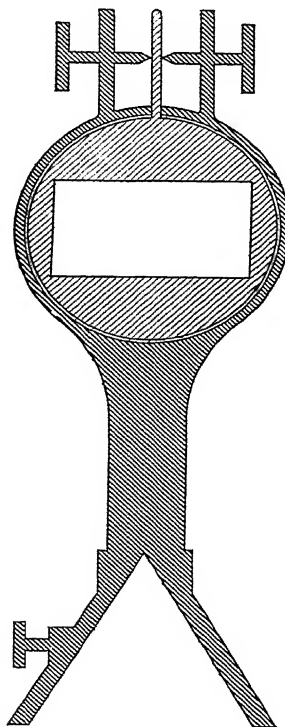
FIG. 2

stigmatic image for a given wavelength. (Cover the wide-open slit partly with a razor blade with a sharp horizontal edge and watch the sharpness of the image of this edge.) If the correct setting has been ascertained for a number of wavelengths, a scale can be put alongside the optical bench so that for further use the position of the lens can be directly determined with the scale.

The cylindrical lens can be employed

with equal success in the Eagle, Paschen, and Rowland mounting, but it acts slightly differently in the three cases. The natural astigmatism for the Eagle mounting is low.[1] Therefore in general only weak cylinder lenses will be necessary to correct it except for the highest orders. There the vertical focal curve will intersect the Rowland circle under a considerable angle, and the correction of the astigmatism is very good only in a very limited region. However, it must be borne in mind that these high orders cannot be reached at all with the Rowland or Wadsworth mounting and only partly with the usual Paschen mountings.

The Rowland mounting with its large astigmatism requires relatively strong cylindrical lenses, but the correction is good over a considerable region. The reason for this is that at the normal the vertical focal curve is parallel to the Rowland circle and therefore can be brought to coincidence with it over a much greater distance than if the two curves intersected under a considerable angle.

For a given Paschen mounting the astigmatism is smallest at the normal and can be most effectively corrected there. Farther away from the normal the correction is good only in a small interval. If the gain in intensity is the only aim, then the correction is sufficiently good over several thousand angstroms (for a 21-foot grating), but for a step reducer or an interferometer it would be good only in an interval of a few hundred angstroms or less. As the plate holder is fixed, the device of putting the plating along the vertical focus rather than the Rowland circle, which is successful with the Eagle mounting, cannot be used here.

Comparison with Other Ways of Removing the Astigmatism. As can be seen from the discussions of the preceding pages there are other ways of removing the astigmatism and some of them have been described and used successfully. Any optical device which produces astigmatism, as a cylindrical lens or a spherical mirror or lens off the axis, can also be used to compensate the existing astigmatism of the concave grating. There is even a way of removing the effects of the astigmatism without any lenses or mirrors simply by placing the light source at a proper distance away from the slit. This method was described first by Sirks[5] as far back as 1895.

We have seen that the vertical focus for the slit falls behind the Rowland circle, which means that, for a given wavelength, there must be a point on the optical axis in front of the slit which has its vertical focus on the Rowland circle. With the help of (4) we find easily that the distance of this point from the slit is

$$R\left(\frac{}{\cos \alpha - \sin \beta \tan \beta} - \cos \alpha \right)$$

or

$$R\left(\frac{1}{\cos \alpha} - \cos \alpha \right)$$

for the Rowland mounting, and

$$R \sin \alpha \tan 2\alpha$$

for the Eagle mounting. A diaphragm, step reducer, etc., will have a sharp image at a wavelength corresponding to this angle of emergence. With this arrangement, of course, no lens must be employed between this point and the slit except a cylindrical lens which acts only in the horizontal plane.

It does not matter whether we put the light source or the diaphragm or whatever else we want a stigmatic image of directly at this point, or produce with spherical or cylindrical lenses or preferably with a combination of both an image which has

its vertical focus at this point and the horizontal focus on the slit. Runge and Mannkopf[6] have discussed several possibilities, and they utilize the dispersion of the lenses to get as extended a region of the spectrum stigmatic as possible. Some of these methods are very effective. However, they make the application of a step slit impossible and have in general the disadvantage that the adjustments have to be made in front of the slit. They are different for each different light source and also for each wavelength region. This makes it impracticable to calibrate the settings once and for all, as is possible with the cylindrical lens between slit and grating. The great advantage of the latter arrangement is that the spectrograph can be used exactly like any other stigmatic spectrograph, without its being necessary to make delicate adjustments in front of the slit which might require the experience of an expert.

There is finally the possibility of placing a cylindrical lens between grating and plate in order to obtain a stigmatic image. For obvious reasons it is practicable to do this only if the lens is placed immediately in front of the plate. This device has been used to increase the intensity of the lines by contracting the length of the line rather than to obtain a stigmatic image. The limitation of this method lies in the fact that the region which can be rendered stigmatic is very small.

REFERENCES

1. G. H. DIEKE, *J. Optical Soc.*, 23, 274 (1933).
2. F. L. O. WADSWORTH, *Astrophys. J.,* 3, 47 (1836).
3. F. ZERNIKE, Zeeman Verhandelingen, The Hague, 1935.
4. W. F. MEGGERS and K. BURNS, *Sci. Papers Bur. Standards,* No. 441 (1922).
5. SIRKS, *A. and A.* 13, 763 (1893).
6. C. RUNGE and R. MANNKOPF, *Z. Physik,* 45, 13 (1927).

A PRACTICAL GRATING SPECTROGRAPH FOR INDUSTRIAL USE

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INTRODUCTION

The title of this paper makes necessary a few remarks concerning definitions before describing the spectrograph itself. The word "spectrograph" we will assume everyone understands; the same will be assumed for the word " grating." By " practical " we mean an instrument which can be placed in the hands of an operator who wishes to use it merely as an analytical tool without bothering to understand the optics or the mechanism inside. " For industrial use " indicates that the instrument should find its greatest field of application in industrial laboratories, especially those wishing to maintain rigid control of materials.

This instrument is not recommended for those laboratories which make only occasional analyses or whose demands are not sufficient to utilize its extreme flexibility and high precision.

The practicability and recognized success resulting from ruling gratings on aluminum deposited on glass made possible the development of a practical spectrograph for industrial use. Until about two years ago, the spoilage rate of gratings ruled on speculum or directly on glass prevented a sufficient supply to fill the demand. There were then a few fortunate possessors of gratings outside the doors of universities who built them into spectro-graphic mountings as accorded their needs and, not to be forgotten, their budgets.

A supply, though limited, of sufficiently good gratings being assured, the problem then was to decide on criteria for the performance of a spectrograph. This step was important. For the first time such an instrument was going out of the laboratory, away from the experts in optics and into the hands of operators who, it was reasonable to assume, know nothing of optics or optical instruments. As an analytical tool the spectrograph had to be simple, rugged, and essentially fool-proof. As an optical instrument, it had to be precise, yet flexible.

The field of spectroscopic endeavor most needing the capabilities of a grating instrument was that of ferrous quantitive analysis. There was also a demand for an instrument giving a fair dispersion in the visible and red end of the spectrum. These requirements, with some modifications and a few necessary compromises, determined the required spectroscopic performance.

CHOICE OF MOUNTING

Sketching briefly why a modification of the Eagle mounting was chosen over the other types of mountings, we can see readily that, since the instrument was to be

built for shipment, such mountings as the Rowland circle (and its special case, the Paschen) and the Rowland mounting (with tracks at right angles) were dismissed immediately on this count, if not for other reasons. This left the so-called parallel light mountings. These, the Wadsworth, Littrow, Pfund, are all complicated by additional mirrors or a lens. The Pfund mounting, beautiful for compact infrared mountings, has far too many parts to make it practicable for an all-purpose instrument. The Littrow requires a good lens as large as the grating, and one of quartz if the ultraviolet is desired. The Wadsworth

This spectrograph mounting is rugged and flexible, allowing a wide range of dispersion with ample resolving power and complete coverage of the spectrum from 2000 A to 10,000 A. It is practically foolproof, requiring a minimum of attention. It is easy to operate for all controls, the plate holder, and the source are within reach of the operator.

CONSTRUCTION DETAILS — MECHANICAL

Fig. 1 shows a schematic diagram of the complete instrument. The optical system consists of a slit fixed in position, a 4-inch 15,000-line-per-inch grating of 3-meter fo-
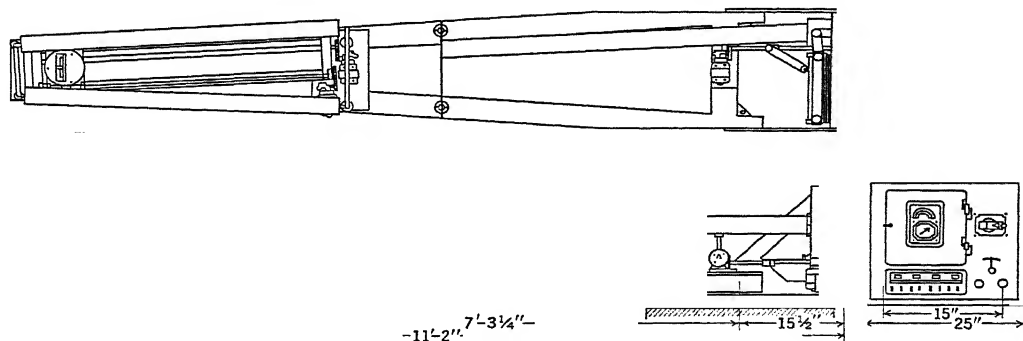
FIG. 1

with its additional mirror proves insufficiently flexible, more bulky, and requires the plate holder at the far end of the spectrograph, away from the source. This mounting works best in a permanent installation. It was deemed desirable that the instrument should be self-contained, compact, and capable of being used in a lighted room.

To review all the reasons leading to the type of mounting finally decided upon would take too long at this time. The modification of the Eagle mounting finally chosen fulfills all the requirements desired.

cal length, and the photographic plate. As such, the optical system is quite simple and is kept down to the smallest number of optical parts. The grating mentioned was chosen, first because 4 inches gives a speed of about f 30 which is ample; second because 15,000 lines to the inch allows a chance for concentrating the light judiciously; third because 3 meters and 15,000 lines to the inch give 5 A per millimeter in the first order, provide a fairly easy curvature to rule, and make the size of the complete instrument practicable for assembly and shipment.

For problems requiring dispersions other

than that mentioned, gratings of finer or coarser spacing might be provided.

A triangle of 4-inch H beams welded together, having webs at the front to support the cassette, slit, and control assembly, provides the base for the mounting. This construction is massive and rigid. The frame is heat treated as a unit after rough machining to remove weld strains.

The complete spectrograph is supported on three points, two at the front and the other a third of the total length from the back end. The weight of the cabinet is carried by the frame, but in such a manner that any twisting cannot affect the optical system.

The slit assembly is mounted in a casting fastened to the front panel and recessed some 4 inches behind the face of the panel. This gives the slit protection from injury. The assembly is arranged so that either an adjustable slit or interchangeable fixed slits may be used. The adjustments pertinent to the slit are made from the front panel both for setting and rotation around the axis of the light beam, the latter for accurately lining up the jaws parallel to the rulings of the grating.

The cassette is hung on two hinges, one above and one below the slit box behind the panel, the centers of which are on a line through the slit jaws. The cassette swings inward for higher-order focus, controlled by an electric motor mounted on the frame and connected through a screw and link arrangement. Within the cassette — at either slide — two screws, one right-handed and one left-handed, driven by a cross shaft at the bottom, serve as guides for the rack and a means for raising and lowering it, carrying the plate holder. These screws are driven by another motor directly connected to the cross shaft, making it possible to position the plate holder electrically.

The plate holder itself is unique in that it contains no felt which can wear and leak light after a period of use. The dark slide is closed normally when not in the cassette. When the plate holder is placed in the instrument, the dark slide hooks over two pins, and, as the plate is racked down, the slide remains fixed, opening more and more of the plate for exposure. After all exposures are made the plate holder is racked back to the beginning position, thereby closing the dark slide automatically. The plate holder itself is of aluminum with the focal curve cast therein; the photographic plate is held against the focal curve by two ribs having the same curvature on the plate holder back. Since a sufficient number of corners are provided for the light to pass around and thereby become trapped, the back can be maintained light proof without felt or the other materials commonly used. The plate holder is placed in the cassette through a door in the front panel, which door is closed during exposures. Since it is quite easy to make such a door light tight, the dark slide, when opened, need not be light tight. The racking is done, as said before, electrically, and automatic stops are provided both at the top and bottom of its run so that it is extremely simple to operate.

The translation and rotation of the grating are also performed electrically. Two motors mounted on the frame at the front of the grating carriage assembly perform these functions. One motor drives the screw which moves the grating forward or backward on the stainless-steel ways; the second through a sliding-key arrangement causes the grating to be turned to the proper angle through a worm and worm wheel arrangement on the grating carriage. These adjustments are controlled from the front panel and allow sufficient precision in setting for the most rigid focusing re-

quirements. Stops are provided also for these motions so that there is never any possibility of jamming a part.

The control panel contains eight switches, two for each of the motions. One provides a fast speed forward and reverse for each of the motions, and the other allows the motors to be slowed down to about one-tenth the normal speed for accurate settings. All calibration points are given on revolution counters which are connected through flexible cables to the part controlled. In each case, the counter drive is independent of the motor driving that part, so that there is no possibility for the calibration to go out because of a failure of a motor or its gearing.

The cassette has mounted on its face an adjustable diaphragm or line mask which allows spectra 1 inch high or any smaller part thereof to be recorded. This line mask is controlled from the front panel and provides a very simple method for superimposing one spectrum on another for qualitative analysis. Exposures are made by means of a remote-control switch which is plugged into the front panel and actuates a shutter mounted behind the slit. In the circuit with this shutter is placed an electric integrating timer for fixing the length of exposures.

FEATURES

A 4-inch grating of 15,000 lines to the inch gives high resolving power and dispersion through the spectrum. In the first order the dispersion is 5 A per millimeter, and a sufficient length of travel for the grating is provided to allow the red of the fourth order to be covered, in which order the dispersion is 1.3 A per millimeter.

The gratings used have a concentration of about 80 per cent of the incident light in the first order, and as a result they are comparable in speed with the large prism instruments. It is possible to approximate the theoretical resolving power of these gratings in all four orders.

Stray light has been reduced to the minimum attainable only in grating instruments. As a result the plates are exceedingly free of background. This is accomplished through efficient light trapping and baffling and as a result the only light reaching the photographic plate is so-called working light.

Standard 4-by-10-inch plates, or films, are generally used, but the plate holder is constructed in such a way that any plate 10 inches long and narrower than 4 inches may be used, or any plate 4 inches wide and less than 10 inches long may be used. This allows considerable saving in plates, if work is being done in a narrow spectral region. The calibration curve is given in such a way that it is possible to know exactly the spectral region in any order covered by the 10-inch plate. The line mask provides a simple means of superimposing spectra, and thereby simplifies the problem of qualitative analysis considerably. Since the plate holder may be racked electrically, it is possible to take moving-plate spectrograms, making possible a technique hitherto difficult. With such a technique, it is possible to study in a very simple way the exhaustion of volatile materials from sources, to determine easily the optimum exposure time necessary to bring out any line, and with such a procedure much can be learned concerning the steadiness and reproducibility of sources.

This mounting is not stigmatic. However, in work requiring stigmatic exposures, the position of the second astigmatic focus for any given spectral region can be fixed; it lies in front of the panel, and by placing step sectors or logarithmic wedges at given

points, it is possible to obtain step spectra over a wide range of wavelengths. That this can be done is shown in Fig. 2.

PERFORMANCE

Using a standard iron arc on 220 volts, 5 amperes, satisfactory pictures are ob-

work, and it is usually necessary to cut it down.

The resolving power of the grating may be seen by referring to Fig. 3. Here we have four spectra in the first, second, third, and fourth orders of the 3100 iron group, taken on the same plate. These lines are
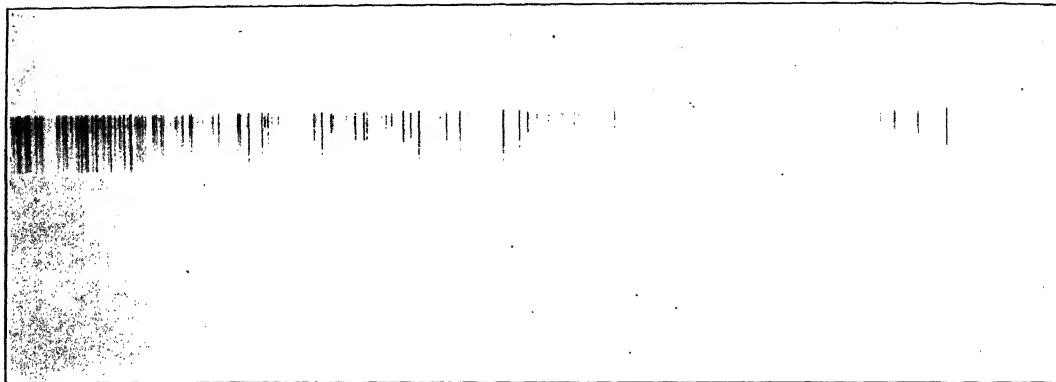
Fig. 2
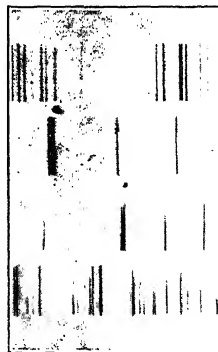
Fig. 3

tained in the first order in about 1.0 second; to get a similar picture in the fourth order with the same arc takes approximately one minute, those exposures being with a 30-micron slit. This speed is more than ample for any quantitative

0.3 of an A apart. A component 0.07 A away is resolved readily in the second, third, and fourth orders.

It can be shown that the ghost intensity in the first order is less than 1/500 the intensity of the parent line. Ghost lines,

of course, appear in all gratings and are not a function in any way of the mounting in which they are used. As a consequence of the low intensity of the ghosts, it is normally not necessary to consider them at all, except in very special cases. The methods of spotting and locating ghosts are now well known, and no trouble results on this score.

With regard to permanence and reproducibility of calibration, it can be said that one of these units has been used in a laboratory containing machine tools and

cause the lines to become fuzzy. It is possible to see how certain lines — for example, magnesium and barium — burn themselves out early in the exposure, and such lines as chromium and cadmium continue full strength for some time; the cyanogen bands remain strong throughout the course of the exposure.

The use of this instrument with step or logarithmic sectors or wedges has been indicated and this is illustrated in Fig. 2. This is a spectrogram of iron in the region 4200 A taken with a logarithmic sector and
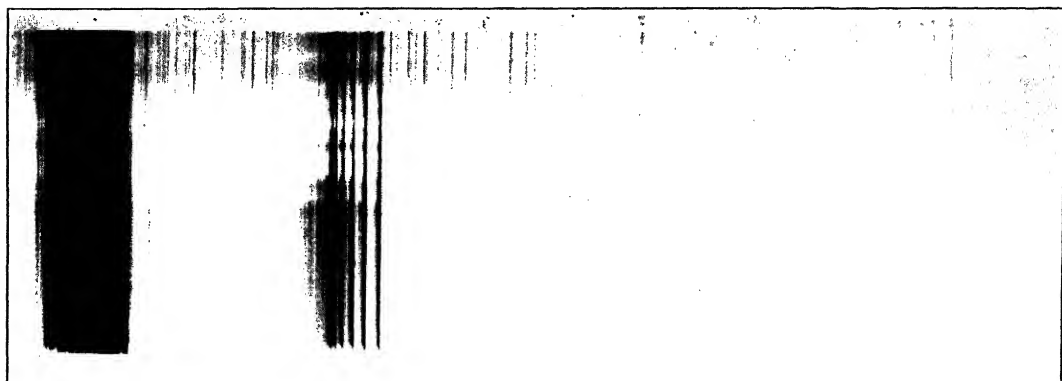
FIG. 4

vibrations of all kinds, and the same calibration has held over a period of nine months. Another instrument was shipped some five hundred miles, and it was found that the first pictures taken were in focus, and subsequent reports indicate that it has remained so.

To illustrate the steadiness and precision of the optical system and the spectrograph as a whole, Fig. 4 shows a reproduction of a spectrogram taken with the plate moving. This picture was taken at the rate of 1 mm per second; it shows that during the time of exposure there was insufficient vibration or erratic motion of the rack to

shows quite distinctly the operation of the sector over the whole length of the plate. Though it is admitted that the instrument will not be completely stigmatic for the whole of a 10-inch plate, it is possible to have it so over the greater portion of the plate. This spectrogram was taken with the sector operating at the correct position in front of the slit. It has been shown that the same type of spectrogram can be obtained by means of a cylindrical lens placed between the slit and grating.

So far as simplicity of operation is concerned, the operator need not move from his position at the panel of the instrument

for racking operations or for moving to a different region of the spectrum. It is completely feasible to take as many as thirty or more spectra on one plate and have them scattered through the different regions of the spectrum in all four orders. It takes about six minutes to go from a focusing position in the first order to a similar position in the fourth order; this time is necessary because the driving motors are geared down to allow precision in setting on the calibration points. Though this may seem a long time, in going from the first to second order only about 15 seconds are required. The ability to slow the motions down from normal speed to 1/10 of this speed with the slow-motion switches makes possible the setting of any one counter to 1/10 of a revolution, and this is adequate for all work normally encountered.

DISADVANTAGES

1. With this type of mounting the instrument is not in focus at all times for all regions of the spectrum. A plate size of 4 by 10 inches allows only 1200 A to be recorded at a time, using a 15,000-line grating. In some instances it is possible to use a grating of fewer lines to obtain less dispersion but a smaller instrument then would perform equally as well. In the Paschen, Rowland, and Wadsworth mountings it is possible to line up several plates at one time and cover more of the spectrum.

2. The slit is recessed. This prevents the use of logarithmic sectors, wedges, directly in front of the slit, but, as has been pointed out, the stigmatic focal point is out in front of the slit except for a region in the ultraviolet of the first order. The recessed slit is an advantage in that this delicate part is protected from accidental injury.

3. The spectrum is not quite normal, i.e., the dispersion is not quite linear. This is also true of all grating mountings except the true Rowland mounting. The effect, however, is small — 0.2A in 3 inches in the green of the first order. This effect is of consequence only in precision wavelength measurements, in which case there are many methods for taking it into account.

4. Ghost lines and overlapping orders are both found in all grating spectrographs. There are simple measures for taking care of each.

ADVANTAGES

1. Small space requirements. Ordinarily the front panel, approximately 2 feet square, is all that is necessary for the operator to touch.

2. This type of mounting can be worked in a lighted room. This is a convenience recognized readily by those who have had to work in dark rooms. It removes the necessity of having to go from the source room into another room to " rack down " or to change to another region of the spectrum.

3. Everything being on the same axis, great rigidity is obtained. External vibrations tend to shake the instrument as a whole rather than one part with respect to another, and as a consequence such vibrations would not affect definition.

4. In precision work where changes in temperature play an important role this mounting can be thoroughly lagged. The advantage here is obvious. Other types of mountings with the same number of optical parts require the whole room to be temperature controlled.

5. The ability to make use of the higher orders, up to and including the fourth, is of some value, especially since there is no

sacrifice of definition. In the higher orders slightly increased dispersion is obtained because the spectra are incident on the plate which is inclined at a small angle. The theoretical resolving power is not changed, however.

6. In the specific mounting under discussion automatic racking provides a means for taking moving-plate spectrograms.

7. It is possible with this mounting to trap completely all light from the zero and higher orders not in use. This means that background is kept at a minimum — an important point in quantitative analysis.

AN IMPROVED DENSITY COMPARATOR

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The ever-increasing demands, especially of the industrial worker, in the field of spectrochemical analysis are bringing forth requirements which could not possibly have been anticipated a decade ago. Then the units available were of a strictly laboratory type used but occasionally and by hands skilled in the art. Today spectrographic equipment is operated, not occasionally by one seeking a higher degree, but perhaps by a high-school student under quite different conditions.

This situation places before the instrument designer an entirely new problem. He must provide a unit which will function day in and day out and give dependable and quickly obtainable results. Many times, also, the instrument must meet space requirements, and must be ready for use when the packing case is removed. In the newer designs lightness and portability must be discarded if these conditions are to be met. Weight properly added is the best means of securing the desired results. Delicately made parts beautifully finished and pleasing to the eye are obsolete and are being replaced almost entirely by heavy castings and rigid structures. Operating parts must be adequately protected from the dirt of the factory; this sometimes leads the designer into a dead-end street since he must sacrifice accessibility for protection. This, in itself, it often not actually an undesirable feature in the design since it leads to a condition in which the danger of tampering by unskilled hands is removed.

It is along these lines that we are working, trying to produce instruments which will function under adverse conditions and give the results desired. In the end those who use the instruments are the deciding majority and we must depend upon them for ideas and criticism. It is practically impossible to incorporate in a single instrument all the ideas which may be offered, and the designer must therefore choose those which appear to represent the majority opinion and which provide for the best optical and mechanical design. We try in our designing to provide the best working unit, one which will meet with general acceptance and provide the maximum of convenience, simplicity, speed, and dependability.

It is with these thoughts in mind that we have designed and built the model of a new density comparator. It is to be remembered that this is a sample instrument and hence is not in production. It is here presented for criticism since changes may be made now which would be impossible when the unit goes into the manufacturing stage.

Fig. 1 shows a front view of the unit and the major part of the mechanical form. The horizontal stage which carries the plate

retained under simple clamps is transported by a screw-driven unit which will be described in detail by a later picture. The screw may be driven either by manual
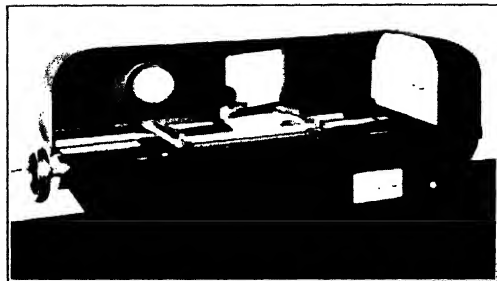
FIG. 1

operation or uniformly by motor. The motor may be engaged or disengaged at will by means of a clutch operated through the lever at the lower right corner. In the present arrangement the motor will carry a 10-inch plate past the optical system in about 25 minutes, a speed reduction which is ample to permit the galvanometer to follow. It is not necessary, however, if widely separated lines are being measured, to traverse entirely by motor. The screw may be disengaged by a thumb release at the corner of the carriage, and this manually moved, free from the screw, to any desired position and instantly re-engaged.

The method by which this is accomplished is shown in Fig. 2. The mechanism is of the worm-gear type, the gear itself being especially built to provide on its sides a double-acting cone clutch. Pressure of the thumb lever releases the clutch and allows the gear to roll freely on the screw. Release of the lever causes a spring engagement of the clutch and rigidly attaches the gear to the carriage mechanism. Thus the gear is in continuous engagement preventing completely the jump attendant

upon a split-nut mechanism, where nut and screw are not exactly in synchronism when the re-engagement is made. The thread is the Acme flat-top type, to prevent damage which might be caused by the sharp 60° type. The screw is relieved at either end so that the gear may run off the worm if the motor is not declutched.

Integral with the screw we have provided a measuring mechanism of a moderately accurate type. This consists of a simple Veeder counter geared to the main screw shaft between the motor and stage. Rigidly attached to the shaft is a divided drum. The counter therefore records rotations of the screw, and the rigid drum measures fractions of rotations. The screw pitch in the present instrument is 2 mm, and so the counter is geared at a two to one ratio and the drum is divided into 200 divisions
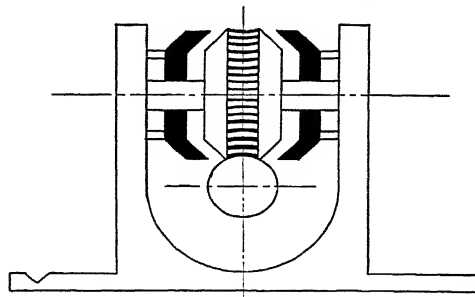
FIG. 2

reading from 0 to 100 twice in each revolution. It is immediately apparent that the reading accuracy is therefore 0.01 mm. We are not making this device to be of the high precision type but are thinking of it only as a device which will provide for interpolation measurements over small ranges. It should be ample for such work as is now accomplished by means of the measuring magnifier.

The optical system is designed for use with the 6-volt 108-watt ribbon filament

lamp. The filament is imaged by a condenser pair in the plane of a rectangular diaphragm in which are two red filters separated by a narrow rectangular clear aperture. The aperture is thus evenly filled by the image of the ribbon. By means of a suitable lens of aperture $f\,2$ this illuminated diaphragm is re-imaged in the plane of the photographic plate, which in turn is re-imaged by a second projection lens upon the receptor screen. We are able by this system to bring the image of the filters exactly into the plane of the plate and avoid the out-of-focus effect of our older instrument. As in the older type a considerable portion of the spectrum is projected upon a white screen in the center of which is the slit over the receptor unit.

In the illumination and receptor system we have followed in general the design of the older unit, though in detail there are several noteworthy changes. The lamp is operated by means of an especially designed Westinghouse voltage-regulating transformer. The lamp is mounted in an external attached housing at the rear, and the regulator is contained within the body of the instrument. The receptor unit is a barrier-layer cell, of the Electrocell type, mounted in a rotatable unit behind the slit in the screen. The entire unit (that is, cell and slit) may be rotated through 90°.

This permits the system to be used for the evaluation of a step calibration pattern without the trouble of plate rotation.

Length of the receptor slit is controllable by means of an elliptical diaphragm immediately behind. The eccentricity of the ellipse is such that the slit may be reduced in length from 1 inch to 0.5 inch. This diaphragm operates from a small thumb screw extending through the face of the slit.

The galvanometer scale has been changed in that the illuminated figures are reflected by the galvanometer mirror to a fixed circular screen in the body of the instrument. The eye is therefore not required to follow the movements of a pointer but observes only the scale divisions in bright figures upon a dark field passing across a fiducial line upon the screen. The scale is illuminated by a Line-o-Light lamp. The galvanometer will have a 2-second period, and even this may be somewhat improved in the final arrangement.

Finally, attention may be called to the mirror by which the screen is viewed. It is placed beside the galvanometer screen and its angle is so adjusted that the screen is easily observed when the eye of the operator is in position to see the galvanometer screen at a normal viewing distance. The lines of sight intersect at about 20 inches in front of the galvanometer screen.

In résumé, the unit is designed especially for rigidity and long life, has a motor-driven horizontally disposed stage, carries as an integral part a measuring device of moderate accuracy, and is especially designed for continuous accurate performance.

A HIGH-SPEED METHOD OF ABSORPTION SPECTROPHOTOMETRY FOR THE RANGE 10,000 TO 2000 A

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All present methods of determining the extinction coefficient of an absorbing material at different wavelengths are limited in range, in speed, or in precision. At first glance it might appear that so rapid, accurate, and elegant a device as the Hardy color analyzer[1] could be considered as giving a satisfactory solution of the general problem of homochromatic spectrophotometry, but this instrument is limited to the region of longer wavelengths, since its principle of operation depends on the transparency of available polarizing materials. For the ultraviolet region simple photographic methods involving density matches are widely used, but though convenient they leave much to be desired in speed and precision.

For some time it has been recognized that an automatic spectrophotometer which would rapidly plot extinction coefficients (or some similar measure of absorption) against wavelength or frequency, over the range 10,000 to 2000 A, would be a very useful tool for biologists, chemists, and physicists. Recently new developments in optical and electrical apparatus have seemed to present the possibility of constructing such a device, and the various parts of a new type of spectrophotometer have now been assembled and tested. Though the entire instrument has not yet been put into operation as a unit, this description is given in the hope that any hidden flaws in the method may be brought to light, or improvements may be suggested.

The proposed method utilizes four pieces of apparatus which have not, it is believed, previously been applied to spectrophotometry. These are: (1) A simple but effective type of concave grating monochromator combining great intensity, unusual spectral purity, and almost constant high dispersion (3.3 A per millimeter) with rapid coverage of the spectral range 10,000 to 2000 A.[2] (2) Photoelectric measurement of intensities by means of the electron multiplier, giving stable d-c amplification of 30,000,000 times, with sufficient output to operate a cathode-ray oscillograph through a supplementary logarithmic amplifier. (3) Use of a cathode-ray oscillograph and motion-picture film for recording, permitting density measurements to be made at the rate of 10 or more per second if desired. (4) Use of an oscillating mirror to shine a monochromatic light beam alternately through solution and blank cells, shifting as many as 60 times per second.

Electrical self-calibration of the system, normally carried out 10 times a second, gives the advantages of direct-reading

methods combined with those of null methods, and eliminates disadvantages of both. Also the system can be calibrated optically at low speed, which calibration then should serve for obtaining thousands of curves at high speeds.

It appears possible to cover the range 10,000 to 2000 A in 100 seconds with resolution to 1 millimicron, or in 20 minutes to 1 A, the results being obtained in the form of a photographed curve of density vs. wavelength.

Optical System. The optical system used is shown in Fig. 1. Light from an incandescent lamp L shines through a hy-
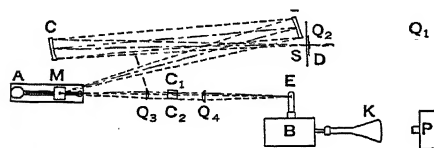
FIG. 1

drogen discharge tube (not shown) to a pair of cylindrical quartz lenses Q_1 and Q_2, arranged so that the first focuses the lamp filament horizontally on the slit, and the second focuses it vertically on the concave mirror C. By this means the slit is filled uniformly with light along its length. The mirror C fills the grating G with parallel light, a mounting suggested by Wadsworth[3] and carried out by Meggers and Burns[4] for a grating spectrograph. The advantages of this mounting appear to be even greater when it is modified for use as a monochromator.

The entrance slit is fixed, the only movements needed to progress through the spectrum being to rotate the grating, and to move the exit slit slightly toward or away from the grating. This system forms a much simpler monochromator of the con-

stant deviation type than can be constructed with quartz lenses and prisms.

The grating is of 10-meter radius with 15,000 lines per inch, so the present monochromator is about 18 feet long. In an instrument built especially for absorption work a 6-inch grating of 15,000 lines per inch and 10-foot radius would probably be found more convenient, the monochromator then being only 5 feet long. The intensity of a continuous spectrum of constant purity varies as the square of the linear dimensions of the monochromator producing it, if all parts are kept equivalent. This explains why such a large instrument as the present one, though operating at only $f35$, can transmit so much light flux. The suggested smaller instrument would operate at $f10$, but with the narrower slits needed to give equivalent purity would give the same light flux as the larger. Since the flux for a given purity depends on the transmitting area times the transmission factor of the monochromator, the modern grating has a decided advantage over the prism. A typical aluminum-coated glass grating has a ruled area of 90 sq cm and will throw 40 per cent of the light which enters its slit into one first order. The usual quartz prism has a transmitting area of not over 30 sq cm, and, because to get freedom from scattered light equivalent to that of the grating monochromator a double prism monochromator must be used, 20 per cent transmission is usually the maximum obtainable. The grating thus appears to have a sixfold net advantage in respect to intensity over the prism. Comparison of angular dispersion gives the grating an additional advantage, for, as the dispersion is increased, widening of the exit slit compensates the loss of intensity, while the entrance slit can also be widened, giving a net gain. As shown in a previous comparison of prisms and

gratings,[5] the standard 15,000- and 30,000-line-per-inch gratings have greater angular dispersions than glass or quartz prisms.

In order to make full use of a large monochromator it is, of course, necessary that its large entrance and exit slits be filled with light. If purity of $\Delta\lambda = 1$ millimicron (10 A) is sufficient, entrance and exit slit widths of 3 mm can be used in the present instrument, and a standard grid-filament projection lamp gives sufficient luminous area to fill these. The hydrogen discharge (to be turned on automatically as the incandescent lamp is extinguished when the region of waves shorter than 4000 A is reached) has not yet been used, but preliminary tests show that it will give sufficient energy for measurements in the extreme ultraviolet.

Instead of an exit slit a small quartz mirror M, 3 by 26 mm, coated on its rear face with chromium and aluminum, is used. This mirror is mounted on the driving motor of a small loud-speaker unit, and is oscillated 20 times a second by means of a square-topped wave, thus throwing the monochromatic exit beam first through the cuvette C_1 containing the solution to be measured, and then through C_2 containing the solvent only. The quartz lenses Q_3 and Q_4 are arranged so that light of any wavelength passing through the cuvettes is approximately parallel. To keep light of every wavelength focused on the electron multiplier E, the mirror is moved along the axis of the lenses to the proper position for each wavelength. This motion at the same time puts the mirror in almost the correct position to get the purest spectrum from the grating, the deviation of the mirror position from the proper position of the exit slit being never more than 1 cm, which corresponds to increasing the band width of the monochromatic exit beam from 1.0 mμ to 1.1 mμ in the present case.

The grating used was ruled by Professor R. W. Wood at the Johns Hopkins University and throws into one first order 80 per cent of the light which emerges from it. Even after all reflection losses of the monochromator are taken into account, 48 per cent of the green light is found in one order. The output of monochromatic green light was found to be about 10,000 times more intense than was needed to give full deflection on a 5-inch cathode-ray oscillograph K through an electron multiplier, and though when an incandescent lamp was used at 10,000 A and 4000 A the intensities were considerably less, they were still ample for full-scale deflection. Pending receipt of an electron multiplier with quartz window, no tests have been made at wavelengths shorter than 4000 A, but preliminary measurements indicate that operation should be satisfactory to 2000 A.
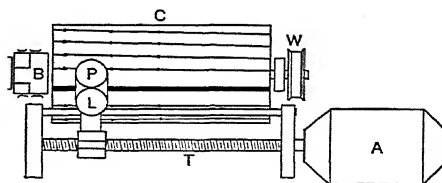
FIG. 2

Photometric System. Just before the light passes into the entrance slit S (see Fig. 2) it traverses a rotating sector disk D, which turns at 1200 rpm (or faster if desired). The axle which turns this disk carries a commutator B and a calibration cylinder C. The commutator feeds current to the oscillating mirror which serves as the exit slit, turning this so that when the entire slit is exposed to light by the disk the light beam will traverse the solution, and when the disk is cutting the length of the slit, the solvent. The disk aperture

varies the length of the illuminated portion of the slit logarithmically with time during three-fourths of the cycle of rotation. To allow for possible imperfections in the disk and optical system, the cylinder C is used to calibrate the light variation by a method described below.

The electron multiplier used is of the electrostatic focusing type developed by Dr. V. K. Zworykin of the Radio Corporation of America, having a noise level less than 10^{-16} ampere, and giving amplifications up to 30,000,000. The output of this multiplier is fed to a logarithmic voltage amplifier B (Fig. 1) which in turn feeds the
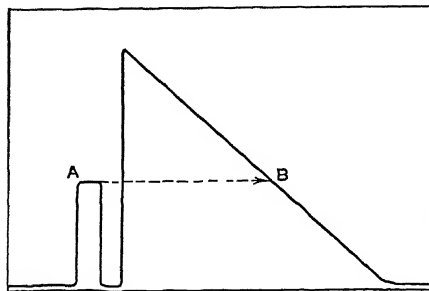
FIG. 3

amplifier of a 5-inch blue screen cathode-ray oscillograph K, RCA type 907. Deflections of the oscillograph are thus made proportional to the logarithm of the intensity of light falling on the multiplier.

Applying a sweep circuit to the oscillograph gives a wave form of the type shown in Fig. 3 as light of any particular wavelength is passed through the two cuvettes. The height of the flat-topped peak A corresponds to the intensity of the light passing through the solution; the inclined portion of the curve calibrates the response of the system, all conditions remaining constant except that the light passes through blank solvent instead of solution. Obviously the density of the solution is meas-

ured by the length of the covered portion of the slit at the point B where the first section of the curve would intersect the second section.

An electrical method could be used to indicate photometric balance, but it was decided that a direct method in which the absorption curve was plotted would be more convenient. The sweep circuit was removed, and the calibrating cylinder C was introduced to control the electron beam of the oscillograph. The sector disk can be set at various positions, and the light introduced into the system can be measured by means of a photocell and galvanometer, in the conventional manner, using light in the 10,000 A region. Dots are then put on a paper wrapped around the cylinder at the positions corresponding to 20 different intensities between 100 and 1 spaced with uniform geometric intervals, as shown in Fig. 2. This process can be repeated at 8000, 6000, 4000, and 2000 A, moving along the cylinder proportionately to the different wavelengths. To a first approximation the plotted points will lie along a series of straight lines parallel to the axis of the cylinder. These lines are filled in heavily with india ink until they are each about 1 mm wide on the 4-inch-diameter cylinder, which is 8 inches long. On the rotational position corresponding to the open part of the sector, when the light is traversing the solution, a heavy black line about 5 mm wide is marked. A photocell arrangement scans the cylinder as it is turned under the beam from a small lamp, and whenever a black line appears the electron beam in the oscillograph, the screen of which is otherwise blank, is flashed on by a pulse from the photocell. As the grating is turned to traverse the exit mirror with the continuous spectrum the photocell moves in wavelength synchronism along the cylinder, the

mirror moves along its screw, and the recording camera P (Fig. 1) photographs the oscillograph record. The result should be a record similar to that shown in Fig. 4. The faint dots correspond to the intensity calibration points on a uniform logarithmic scale; the heavy dots give the densities of the solution.

Since the intensity of the light and the sensitivity of the multiplier system vary widely with wavelength, it is necessary to control these if the calibration lines of Fig. 4 are to be reasonably horizontal and straight. This it is planned to accomplish by a combination of pre-controlled light-intensity variation with automatic am-
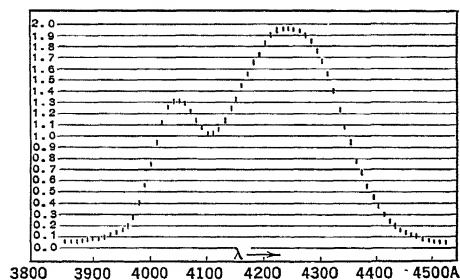
Fig. 4

plification control of the output of the multiplier. Constancy of maximum deflection to 1 per cent should be sufficient, since this will give curves of good appearance, and even with much larger variations correct values of the extinction coefficient can be read from the background calibration lines. Errors from incorrect cutting of the sector disk and non-uniformities of optical parts are eliminated by the calibration method, except as the slits (exit mirror) may vary in transmission (reflection) with time along their lengths. Probable chief sources of uncertainty appear to be the exit mirror (which has, however, been carefully made of crystal quartz pro-

tected by a rear coating of lacquer) and the fact that the light beam strikes the electron multiplier from two slightly differing aspects through the two cuvettes.

Whether the variation in transmission of the monochromator along its entrance slit and exit mirror will continue constant over long periods of use remains to be seen, but recalibration oftener than once every few thousand runs should not be necessary provided dust is kept off the mirror. A quartz window is provided in front of the mirror to insure this.

The light source used must vary in intensity but slowly with time, unless a quick-acting automatic control is installed to keep it at the correct brightness. If the spectrum is to be run through rapidly, narrow spectrum lines or other intensity discontinuities must be avoided in the source, unless the grating is rotated discontinuously. In the present monochromator the range 10,000 to 2000 A is traversed by means of an electric drive in 100 seconds, so that one measurement is made every 8 A when the calibrating disk is run at 10 turns per second. Autosyn motors are used to keep the photocell calibrator, the exit mirror, and the camera in wavelength synchronism with the rotation of the grating. If a smaller monochromator were used these could conveniently be driven together mechanically instead of electrically.

By means of suitable cams in the drive mechanism the output curve could be plotted on a uniform wave number instead of wavelength scale.

The absorption cuvettes are of clear fused quartz of 1-inch diameter, and can be of any thickness up to 10 inches. If cuvettes whose thicknesses are integral multiples of 1 cm are used the output curves will give extinction coefficients directly, or fresh charts which will fit any

cuvette thickness can be wrapped around the calibration cylinder.

The greatest advantage of the proposed system appears to be its flexibility. Though it may appear somewhat complex, many simplifications can be introduced by sacrificing speed or precision or convenience. The system as described is no more costly than a large double monochromator, a large quartz prism spectrograph, or some commercial recording microphotometers. The monochromator can be used also as a high-speed, high-dispersion spectrograph. The vibrating light-beam method also lends itself to improvement of several of the photographic systems of absorption spectrophotometry, as will be described elsewhere.

REFERENCES

1. HARDY, *J. Optical Soc. Am. and Rev. Scientific Instruments,* **18**, 96 (1929); *J. Optical Soc. Am.,* **25**, 305 (1935).
2. HARRISON, *ibid.,* **28**, 49 (1938).
3. WADSWORTH, *Astrophys. J.,* **3**, 54 (1896).
4. MEGGERS and BURNS, *Natl. Bur. Standards Sci. Paper* 441 (1922).
5. HARRISON, *Proc. Fifth Conference on Spectroscopy, 1937,* p. 31 (1938).

STANDARD HELIUM LAMP FOR MEASURING INTENSITIES OF SPECTRAL LINES

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As a result of the work of Ornstein, Dorgelo, Hansen, and others, methods have been developed by which the relative intensities of spectral lines can be accurately measured. The methods employed are photometric, and the apparatus and technique have been improved until very satisfactory precision is possible. The measurement of the absolute intensities of spectral lines is a much more difficult problem and one which has not as yet been satisfactorily solved. Fortunately, for many purposes, the measurement of the relative intensities suffices. A great deal of new research has been made possible, especially in the field of electrical phenomena in gases, because of these developments, and a tremendous new impetus has been given to the field of spectrochemical analysis by the development of methods for measuring the relative intensities of spectral lines. Since 1925, when Gerlach introduced the method of internal control into this field, there has been an ever-increasing tendency to base analytical methods upon the measurement of the relative intensities of spectral lines until now these are the prevailing ones. Much of the improvement in technique and apparatus has resulted from the demands for greater analytical precision.

Two methods for measuring the relative intensities of spectral lines are in especially wide use. They differ in the way in which the relative densities of the images on the photographic plates are converted into relative intensities of the spectral lines through the laws of the development of images in the photographic emulsion. The general type of relationship between the density of the image and the exposure of the plate is well known. It is necessary for measurement to determine the function which expresses this relationship for the particular plate and spectrum under consideration. One method makes use of a rotating sectored disk in front of the slit of the spectrograph which varies the time of exposure over different parts of the slit. The other method employs a stepped slit or diaphragm in front of the slit which varies the exposure for different parts of the image. Both methods give satisfactory results. In some cases it has been found that the conditions of excitation of the spectra are sufficiently well controlled so that the lines have the same relative intensities in different spectrograms. Then, when a sufficient number of lines are present, one can use the relative intensities of selected lines measured by one of the foregoing methods for the calibration of subsequent spectrograms photographed from the same source.

Some recent research by one of us (O.S.D.) and Mr. O. G. Koppius in this laboratory suggested to us that it should be possible to make a simple lamp whose spectrum lines would have constant relative intensities over a long period of use. Because of the clean-up of most gases in discharge tubes, we naturally considered using one of the rare gases because it is well known that if cathodic sputtering is avoided the rate of clean-up of the rare gases is extremely slow, and such a lamp should remain constant for a long time. Metallic vapors were also considered, but these are more difficult to handle and the vapor pressure is not constant unless care is exercised in the operation of the lamp. The lamp to be described in this paper is filled with pure helium.

There are several advantages to be gained by using a standard lamp. Its cost should not be excessive, and the only additional equipment needed is a neon-sign-type transformer to excite it. In chemical plants and laboratories where metal parts are subject to corrosive vapors, the lamp would eliminate care and replacement of metal apparatus. As the spectrum of the lamp would be photographed through the same slit as the spectrum of the analytical source, no changes would have to be made in the slit of the spectrograph and a fixed slit could be employed.

The lines used for calibrating a plate must lie in a region of constant contrast of the emulsion. This is a disadvantage where the contrast varies rapidly with the wavelength. The spectrum of neon and that of argon are rich in lines in certain regions, but the spectrum of helium has so few lines that a wider spectral range is covered by the lines used for calibration. We have employed lines between 2829 and 3867 A, and a typical calibration curve is shown in Fig. 1.

One distinct advantage in the use of a standard lamp is that the spectral lines of the lamp may serve as external standards as well as for calibrating the plate. If an analytical source can be standardized well enough so that the relative intensities of the spectral lines in different exposures remain constant for a given specimen, as
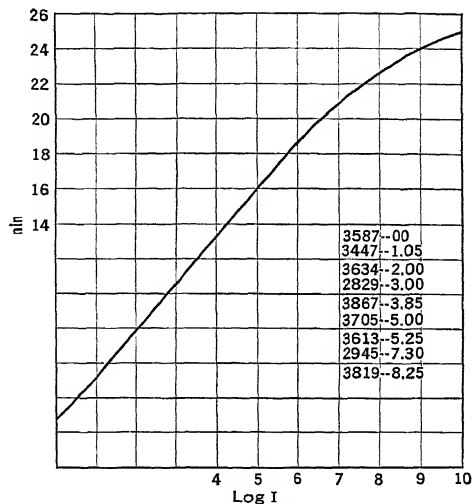
FIG. 1

is true of the best sources now employed for analytical work, then an external standard may be employed. The standard lamp may be set so that its spectrum is photographed simultaneously with that of the specimen being analyzed and the same procedure followed as in the method of internal control. The external control would, of course, not be subject to influence from materials not present in every specimen or to changes in intensity due to interference from elements that vary in amount from specimen to specimen. Some of the complications due to such interferences are avoided if the lines of the test element alone are subject to such influences and

not both those of the test element and of the internal control. In the analysis of gases, the relative intensities of spectral lines of different elements are often found to be extremely sensitive to changes in total pressure and to changes in the pressure of one of the constituents not being measured. Such disturbances have been a big hindrance to the development of spectroscopic methods of quantitative analysis of gases. While they have been avoided over certain pressure ranges in some cases, as is pointed out in another paper by the writers, so that an internal control can be employed, the use of an external control may often be found to be advantageous.

The lamp that we have employed is a simple glow discharge tube with a quartz capillary 3 mm in diameter and 5 cm long. The electrodes are hollow nickel cylinders 15 mm in diameter and 3 cm long. They are sealed into Pyrex bulbs with tungsten lead-in wires. The electrode bulbs are sealed onto the quartz capillary with graded seals, and the whole lamp is about 18 cm long.

In forming the lamp, the electrodes are first thoroughly outgassed by means of induced eddy currents; then spectroscopically pure helium is introduced to a pressure of 0.5 mm. A getter (barium) pellet is inserted into a side tube sealed onto the discharge tube and is flashed after the electrodes are outgassed. The helium is introduced very slowly through a liquid-air trap so no mercury vapor is carried into the lamp. It is very important to exclude mercury vapor completely. After the helium is introduced, the lamp is operated for a considerable time while it is still connected to the pumping system and getter tube so as to remove the last traces of impurities (in our case 18 hours). If the spectrum shows no impurities, the tube is

now sealed off the pumping system with the getter tube attached to it and the lamp is again operated for a long period (36 hours) and again tested. If the spectrum is pure, the getter tube is sealed off and the lamp is complete. The spectrum should contain no trace of any but helium lines.

The lamp was tested for constancy over a wide range of conditions of operation. The primary voltage of the neon-sign-type transformer was varied from 60 to 110 volts and no change could be detected in the relative intensities of the lines. Then the voltage applied to the lamp was varied from 800 volts to 12,500 volts and again the lines showed constant relative intensities. A condenser of capacitance 0.01 microfarad connected in parallel with the lamp produced no change in the relative intensities of the lines. Tests were likewise

TABLE I

Wavelength	$\text{Log}_{1.6}\ I$ (Arbitrary Scale)
2829	3.00
2945	7.30
3447	1.05
3587	0.00
3613	5.25
3634	2.00
3705	5.00
3819	8.55
3867	3.85

wise made on the constancy of the lamp over a long period of operation. Exposures of the same duration were made intermittently on the same plate over a period of six days during which time the lamp was operated continuously. After the plate was developed, the densities of the several lines were measured and were found to have a maximum deviation from the

mean of 2.4 per cent. Consequently, it was concluded that the lamp could be used as a standard by which the total integrated intensities (energies) of spectral lines might be compared.

The lines used for the calibration of photographic plates and their relative intensities are given in Table I.

A curve showing these relationships is given in the figure, and it will be noted that a complete calibration curve extending beyond the straight-line portion at both ends can be obtained from the lamp. An exposure of 1 minute on an Eastman Polychrome plate with a Hilger E2 quartz spectrograph was found to be adequate. The lamp and spectrograph must always have the same relative position.

APPLICATION OF ISODENSITY CONTOURING METHODS TO SPECTRUM PHOTOMETRY

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The term spectrum photometry will be used to denote the determination of spectral-energy distribution or the intensity of spectral lines or regions. The term spectrophotometry can then be reserved for the determination of spectral transmission and reflectance and related problems, in which connection it is more commonly applied. Photographic spectrophotometry, so defined, will not be considered in this paper.

In 1907 C. E. K. Mees[1] introduced the wedge spectrograph as a method of photographic sensitometry. In this instrument a wedge or thin prism of gray glass, cemented to a wedge of clear glass of similar refractive index to form a plane block, is mounted almost in contact with the spectrograph slit. The wedge is placed with its vertex at one end of the slit, the thickness of the absorbing glass increasing along the slit length. If provision is made to illuminate the slit uniformly in the absence of the wedge, a spectrum photograph made with the wedge in place will, in general, exhibit spectrum lines of varying length, the longer lines being the more intense. The familiar wedge spectra showing the approximate spectral sensitivity of photographic plates are made in this manner. It is evident that the same device may be used as a method of photometry of the spectrum. Merton[2] has applied it

extensively to certain spectroscopic problems.

In 1906 Belin[3] proposed the so-called logarithmic sector disk as a sensitometric

$$h = a + \log_{10}\left[\frac{\theta}{2\pi}\right]$$
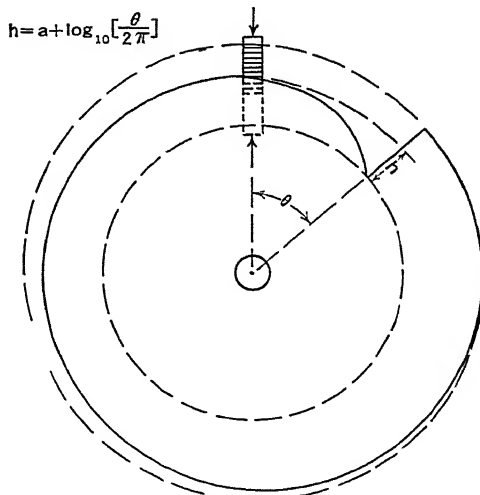
FIG. 1

method. The optical density of an absorbing prism varies as a linear function of the thickness, hence of the distance from the apex. To secure a similar effect with the rotating sector it is necessary to use a metal disk with its profile cut in the form shown in Fig. 1. When the disk is mounted before a spectrograph slit and rotated at uniform angular velocity, it will be evi-

dent that a point on the slit a distance h above the end will be illuminated for a fraction of the period of rotation proportional to the antilogarithm of h. Thus the rotating spiral will introduce, in effect, an optical density varying in a linear manner with distance along the slit. The rotating spiral possesses the advantage that its action is independent of wavelength, a condition impossible to meet over any considerable spectrum range in the case of the glass wedge and difficult with wedges of other materials. On the other hand, the rotating spiral possesses the disadvantage of a moving part which must be maintained in accurate alignment.

Holst and Hamburger[4] in 1918 again proposed the Belin spiral, apparently unaware of Belin's work. In 1929 Scheibe and Neuhäusser[5] applied the rotating spiral to spectrum analysis, and O'Brien[6] used a modified form for the photometry of the ultraviolet solar spectrum.

Photographically the absorbing wedge and the rotating spiral sector are equivalent provided that the constant intensity but interrupted variable time exposure produced by the sector is photographically identical with the variable intensity constant time exposure produced by the wedge. Weber,[7] Howe,[8] Weinland,[9] O'Brien,[10] Webb,[11] and others have investigated this point. It has been shown that the interrupted exposure through the sector is photographically equivalent to the continuous exposure through the wedge, provided that the interruption frequency is sufficiently high. The minimum frequency depends upon the light intensity, but for ordinary spectrograph exposures lasting a number of seconds a frequency of 50 or more interruptions per second is adequate.

A portion of a wedge spectrum of the mercury arc in quartz is shown in Fig. 2. A wide slit has been used, and the two ex-

posures are in the ratio of 20 to 1. The apparent height of any line is proportional to the logarithm of its photographic intensity. It is worth while to compare this method of intensity measurement with the more common procedure involving deter-
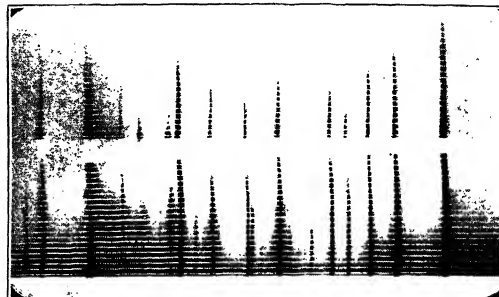
Fig. 2

mination of the optical density of a photographic image, and calculation from it of the light intensity which produced the image. This calculation is dependent upon a calibration or characteristic curve for the plate, and since this characteristic curve depends upon the exact conditions of development, it is usually necessary that a complete series of calibrating exposures be carried on each plate. The labor involved in determining the densities of the calibration exposures as well as the unknowns, and the construction and use of the characteristic curve, is considerable. Compared to this the wedge spectrum is in a sense direct reading for intensity, and requires no calibration for relative, and only single-point calibration for absolute, intensity.

The convenience of the wedge spectrum is obtained, unfortunately, at a certain sacrifice, since the coordinate along the surface of the plate perpendicular to the dispersion coordinate must be devoted to the intensity measurement. The method

involving the measurement of density, on the other hand, utilizes, in effect, the depth coordinate in the emulsion, since the amount of silver per unit area of the image provides the measure of intensity. This leaves one coordinate free to represent any other variable, which may be a matter of considerable convenience. The determination of changes in spectral intensity along some line across the surface of a light source is an example of this. Fortunately in the majority of applications a third coordinate is not required and the wedge spectrum can be applied.

It is important to know whether the obvious convenience of the wedge method is secured at a sacrifice in accuracy as compared with the more laborious procedure. The reading of intensity from such a spectrum photograph involves, directly or otherwise, the determination of a contour line of constant photographic density. The height of this contour above a base line is, at any wavelength, a measure of the logarithm of the photographic intensity of the light falling upon the plate. Two steps are thus involved.

1. The height of an isodensity contour must represent some function (usually the logarithm) of the photographic intensity.

2. The position of such a contour must be determined and its height above a base line measured.

The first requirement under 1, above, in the production of a wedge spectrum, is that the illumination of the spectrograph slit be strictly uniform before the wedge or rotating sector is introduced. Included in this is uniformity of slit width which affects the illumination of the photographic plate even with a pure line spectrum because of the finite resolving power of the photographic emulsion. The conditions necessary to secure such illumination involve standard optical procedures and will not be considered here. The next requirement is that the gradient of the wedge be either uniform or known throughout its length. If a rotating spiral is used in place of a wedge its profile must be cut to the required accuracy and the alignment of its axis of rotation maintained. In a gray glass wedge uniformity of gradient is easy to secure since it is only necessary that the sides of the thin glass prism be polished plane. Since glass can be used over but a limited spectral range there has been a need for other types of absorbing wedges. Merton[12] and others have used optical wedges of sputtered platinum on quartz. These are nearly non-selective with wavelength and permit working far into the ultraviolet, but unfortunately the gradient is not linear and this adds greatly to the labor of reducing results. Wedges of aluminum evaporated on quartz have been described by O'Brien and Russell.[13] These are substantially non-selective with wavelength as are the sputtered platinum wedges, and they have the further advantage that the gradient can be made uniform to a high order of accuracy.

The second requirement under 1 is that the photographic plate respond uniformly over a considerable area. This requirement is not peculiar to the wedge method. Irregularities in response due to development can be eliminated by several techniques, among which brush development is very convenient. In general, it is desirable to carry development as far toward gamma infinity as possible without serious fog. In this way small variations in uniformity of development are made of less importance. The high gamma resulting from such a procedure is sometimes objectionable in the classical method of photometry involving density measurement, but

is an actual advantage in the wedge method. Apart from development irregularities small variations in sensitivity exist over the surface of a photographic plate. These variations are, in general, much less on film than on plates, owing to the method of emulsion coating. Where results of high accuracy are required uniformity tests should be made with the actual emulsion and conditions of development in use.

The principal difficulty involved under 2 above is the determination of the precise points on a wedge spectrum which are of constant photographic density, that is, in the determination of an isodensity contour line. Once determined, the measurement of height of the contour above a reference base is simple. On superficial inspection of a wedge spectrum such as shown in Fig. 2 the length of the lines is a fairly definite quantity, the "length" being, of course, the distance from the base of the spectrum to the point where the spectrum line appears to vanish. If one observes the latter point under some magnification, however, it is evident that the photographic image trails off with gradually decreasing density without definite termination. The higher the gamma to which the plate is developed the more definite this line termination becomes, but necessarily the termination occurs at low density near the toe of the characteristic curve where the slope is never very great, so that the uncertainty in line length remains considerable. Merton[14] has suggested several methods for rendering the determination of the wedge spectrum line more definite, and methods have been described by O'Brien,[15] O'Brien, Mohler, and Stewart,[16] and Foster[17] for photometric comparison near the ends of a line. Although these add somewhat to the accuracy they leave much to be desired.

An obvious method of improving the contrast near the end of a wedge spectrum line is to make a photographic print upon an emulsion of very high contrast. This method[18] has been used in photographic laboratories but is generally mistrusted in spectroscopic work because of the added photographic manipulations. However, if extreme contrast can be secured without complicated procedure or loss of accuracy the advantage is considerable, so we have investigated the matter in some detail,[19] using a commercial Eastman emulsion known as Kodalith. In an ordinary developer this emulsion exhibits a fairly high gamma, but in a special class of developer as represented by Eastman formula D-85 a gamma in excess of 8 can be obtained. Such developers have poor keeping quality, which is inconvenient, and act so rapidly as to increase the difficulties in securing uniform development. Simple dilution, while decreasing the rate of development, lowers the attainable gamma and has other disadvantages. Recently a developer more satisfactory for our purpose has been produced by Mr. Thomas Finucane* of this laboratory.

The effect of high-contrast printing is

*Details will be published by Mr. Finucane in the near future. We are indebted to him for the following formula which he considers tentative, but which has given good results.

Potassium bromide	6.3 grams	
Sodium bicarbonate	290 "	A
Sodium sulphate	180 "	
Hydroquinone	60 "	
Paraformaldehyde	48 "	
Water to make	4 liters	

Mix and dissolve group A in about 3 liters warm (30°) water, then add hydroquinone and dissolve (1) by bubbling nitrogen through or (2) by shaking with nitrogen rather than air in bottle. When dissolved, repeat operation with paraformaldehyde. Always keep nitrogen atmosphere above developer while in stock bottle. Use at 18–19° C. Development time approximately 6 minutes.

shown by the tone reproduction diagram of Fig. 3. Suppose that the original negative material upon which the spectrum is recorded has a gamma of unity. The char-
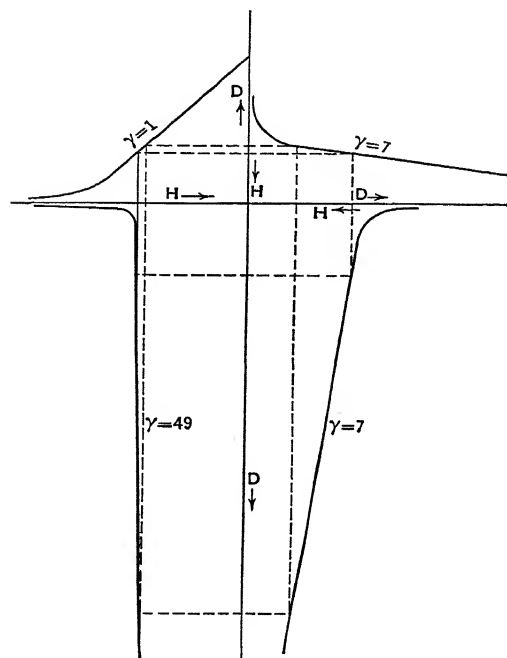
FIG. 3

acteristic curve for this material is shown in quadrant I where H represents the logarithm of the exposure and D the optical density of the resultant image. Consider a small increment in H as shown by the dotted lines. This will result in a similar small increment in D since the slope (gamma) is unity. Rotating Fig. 2 counterclockwise through 90° and viewing quadrant II, we have the characteristic curve for the photographic positive material assumed for illustration to have a gamma of 7. The D-scale of the negative material becomes the H-scale of the positive, and

the corresponding increment in D for the positive is seven times the increment in D for the negative. Rotating the diagram again 90° counterclockwise and viewing quadrant III we have again shown the characteristic curve of a material with a gamma of 7, but used this time to print a duplicate negative. The D-scale for the positive becomes the H-scale for the duplicate negative, and the increment in D for the duplicate negative will be seen to be 49 times the increment in D on the original negative to which it corresponds. In quadrant IV is plotted the equivalent characteristic curve for the over-all process involving original negative of gamma unity, positive print of gamma 7, and duplicate negative of gamma 7. The over-all gamma in this case is 49.

As a practical matter it is desirable to adjust the exposure in making a duplicate negative so that a part of the toe of the curve for the duplicate negative is included. This gives a clear fog-free background above the wedge spectrum, but involves some sacrifice in contrast. This is not serious since we are able to obtain a gamma as high as 15 with the new developer, so that an over-all gamma as high as 225 is theoretically possible with the double printing. We may thus fall considerably short of this figure, utilizing the toe of the curve for the duplicate negative material, and still obtain an extreme contrast. Kodalith film (ordinary, not orthochromatic) is used for both positive and duplicate negative.

A duplicate negative of the spectrum of Fig. 2 prepared in this manner is shown in Fig. 4. Although the difference in appearance between 2 and 4 is minimized by the half-tone reproductions, it is still sufficiently marked. The wedge spectrum profile terminates as abruptly as though formed with a stencil, establishing a sharp iso-

density contour line of the original negative. The height of this contour above the base line is most rapidly determined by
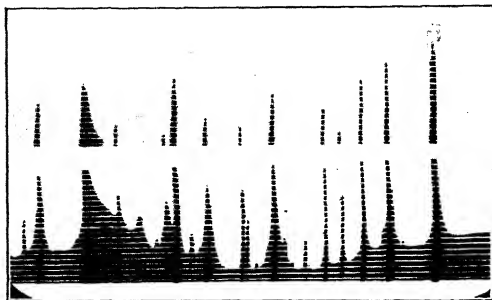
Fig. 4

reading directly from the intensity scale formed in the spectrum by interruptions in the original spectrograph slit.[20] The space between adjacent interruptions in Figs. 2 and 4 corresponds to a difference in $\log_{10}$ (intensity) of 0.1.

Any irregularities in the sensitivity of the positive material will be superimposed upon those of the original negative and carried through to the final duplicate negative from which intensities are read. It is important to determine the magnitude of these irregularities. A test of the uniformity of Kodalith film is shown in Fig. 5. A neutral dyed gelatin wedge of very low gradient was contract-printed to Kodalith film with suitable precautions to assure uniformity in the printing illumination. This is reproduced at unity gamma in strip A of Fig. 5. Each strip in the original photograph from which Fig. 5 was made had a width of 1 cm. On this scale the gradient of the original wedge represented by Fig. 1 amounted to a density difference of only 0.09 per cm along the strip. A contact print from the wedge to Kodalith was again contact-printed to Kodalith, making in effect a duplicate negative of the original wedge. The re-

sult is shown in strip B. The increase in contrast follows as anticipated, but it will be noted that the contour line of constant density across strip B is not straight. To determine whether this departure from the straight line is a defect in the Kodalith film, a second contact print (positive) was made from the wedge to Kodalith and a duplicate negative made from this, using another tray of developer. The result is shown in strip C. It will be seen that the isodensity contour across strip C is identical with that across strip B to a high order of accuracy. The defect, then, was not in the Kodalith reproduction but in the original dyed gelatin wedge, although too slight to be detected by visual inspection of the original wedge. A similar pair of experiments were conducted on the same wedge but at a different exposure level to produce another isodensity contour line at another level across the wedge. The results of these experiments are shown in strips D and E. The identity of these again confirms the dependability of the Kodalith film and the development procedure.

An estimate of the precision of this method for determining a density contour can be made from the above test. The contours on strips B and C differ at no place by as much as 0.5 mm, which is also true of the contours of strips D and E. Referring to the gradient of the original wedge it follows that these reproduce the isodensity contours of the original within a total spread of 0.0045 density. Thus the film with this development procedure is certainly uniform within 0.0045 in $\log_{10}$ (exposure), so that an intensity measurement may be made with this precision so far as the Kodalith reproduction is concerned.

Errors due to non-uniformity in the original negative material may be greater. Film coatings such as positive motion-pic-

ture stock we have found uniform within 0.02 density when developed to a gamma of 2.3. Referred back to exposure this is equivalent to $\log_{10}$ (intensity) of 0.009 or the same order of performance as is shown by the Kodalith. Few if any negative film

of intensity from the characteristic curve, it is evident that there is no choice in the ultimate precision of the two methods. The speed and convenience of the wedge method are marked, however, and the precautions necessary to secure a given pre-
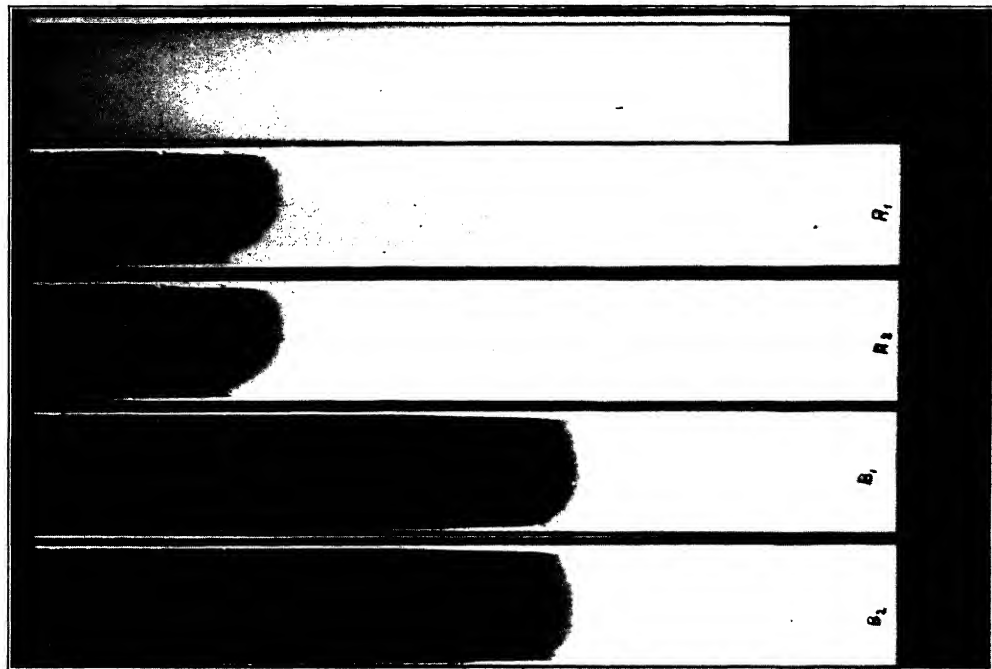
Fig. 5

materials behave as well, and no plate coatings within our experience can compare with such film performance.

We may conclude that spectrum intensity measurements, when made by the wedge method with high-contrast contact printing as described above, are limited in ultimate precision only by the uniformity of the photographic material upon which the original exposures are made. Since the same is true of the classical method of photographic photometry involving the measurement of density and the calculation

cision are certainly not greater than those of the classical procedure.

One application of the foregoing is of sufficient interest to warrant brief mention here, and will serve as an example of the convenience and power of the wedge spectrum method. This has been described in outline previously.[21] In the measurement of the ozone in a zenith atmosphere by spectroscopic means it is necessary to measure the intensity at two or more wavelengths in the solar spectrum which are differently absorbed by ozone. To follow

changes in oxone content it is desirable that such measurements be made several times per hour throughout each day, and

motion-picture-film with a special type of automatic wedge spectrograph.[22] These are contact-printed to perforated Kodalith

A   B
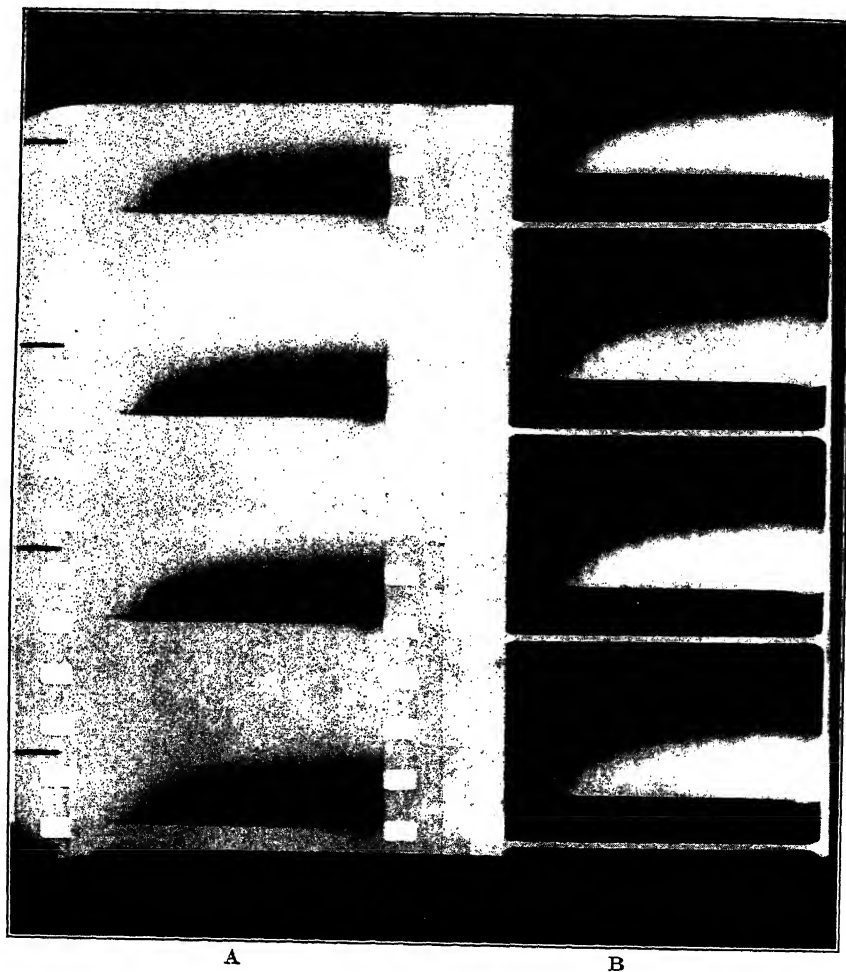
FIG. 6

an automatic method providing a permanent record is of value.

In Fig. 6A is shown a series of exposures at the ultraviolet end of the solar spectrum made three times per hour on 35-mm

film in a motion-picture mechanism providing accurate register, and are reproduced in Fig. 6B. The 35-mm Kodalith film strip is next projection-printed to Kodalith paper 4 inches wide and intermit-

tently fed from a roll in an apparatus with an optical system as shown in Fig. 7. This consists of a projector which permits isolating any pair of spectral lines or narrow regions from the wedge spectrum and imaging them side by side upon the paper. The
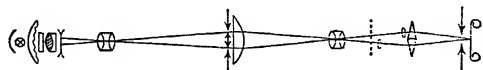
FIG. 7

35-mm Kodalith positive is produced in a contact printer where uniformity of illumination is easily secured. Only approximate uniformity of illumination is required for the second printing in the projector, and this is accomplished by an absorbing field correcting plate. The final result is shown in Fig. 8, each pair of lines representing the logarithms of intensity of a selected pair of lines in the solar spectrum. The two series of exposures shown in Fig. 8 were made from the same negative film for one day's run, but at two different pairs of
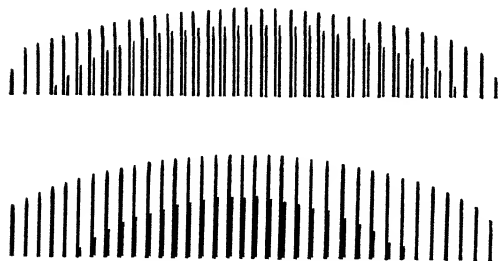
FIG. 8

wavelengths, each pair providing an independent determination of the atmospheric ozone. The difference in length between the two lines of a pair which is easily measured directly on the paper with a transparent scale is proportional to the log

of the ratio of intensities at the two wavelengths and is the quantity used directly in the calculation of ozone. Both spectrograph and projection printing mechanism have been made entirely automatic and yield a permanent record which may be rechecked at any time.

This system of ozone recording has been made possible by the wedge spectrum and contouring methods, but is only one of many applications of a very useful photographic procedure.

REFERENCES

1. MEES, *Brit. J. Photog.,* **54,** 384 (1907).
2. MERTON, *Chem. Soc. J.* 103, 124–127 (January, 1913).
3. BELIN, *Brit. J. Photog.,* p. 630, August, 1906.
4. HOLST and HAMBURGER, *Proc. K. Akad. Amsterdam,* 20.7, 1021–1024 (1918).
5. SCHEIBE and NEUHÄUSSER, *Z. angew. Chem.,* 41, 1218–22 (1928).
6. O'BRIEN, *Phys. Rev.,* 33, 640 (1929).
7. WEBER, *Ann. Physik,* **45,** 6, 801–838 (November, 1914).
8. HOWE, *Phys. Rev.,* **8,** 674–688 (December, 1916).
9. WEINLAND, *J. Optical Soc. Am.,* **15,** 337 (1925).
10. O'BRIEN and O'BRIEN, *Phys. Rev.,* 37, 471 (1931); O'BRIEN and PARKS, *ibid.,* 43, 1052 (1933).
11. WEBB, *J. Optical Soc. Am.,* 23, 157, 1933.
12. MERTON, *Phil. Trans. Roy. Soc.,* 216, 459–488.
13. O'BRIEN and RUSSELL, *J. Optical Soc. Am.,* 24, 54 (1934).
14. MERTON, *Phil. Trans. Roy. Soc.,* 216, 459–488 (June, 1916); 99, 78–84 (April, 1921).
15. O'BRIEN, *Nat. Geo. Soc. Contributed Technical Papers,* Stratosphere Series, 2, 49 (1936).
16. O'BRIEN, MOHLER, and STEWART, *ibid.,* 2, 71 (1936).
17. FOSTER, *Proc. Roy. Soc.,* 123B, 422–430 (August, 1937).
18. LUTHER, *Brit. J. Photog.,* 57, (1910); HIGSON, *Phot. J.,* February, 1921.
19. O'BRIEN and STEWART, *J. Optical Soc. Am.,* 28, 50 (1938).
20. O'BRIEN, *Phys. Rev.,* 33, 640 (1929).
21. O'BRIEN and STEWART, *ibid.,* 53, 949 (1938).
22. STEWART and O'BRIEN, *ibid.,* 53, 949 (1938).

A SIMPLE METHOD FOR TESTING DISPERSION FILTERS

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Dispersion filters were suggested by the Danish physicist Christiansen[1] 55 years ago, but they did not stand the test of practical use before the experiments on photodichroism[2] were carried out with the filters in my laboratory in Leipzig.

The principle is well known. If one mixes a suitable coarse-grain powder of a transparent isotropic solid, for instance glass, with a suitable organic liquid, the dispersion curves of the solid and the liquid intersect each other at a wavelength λ_0. The mixture behaves for this wavelength like a homogeneous transparent medium. Other spectral ranges than λ_0 are more or less scattered or dispersed. By placing a trough with plane end plates filled with the mixture near a lens, the filament of an incandescent lamp or any illuminated diaphragm is imaged sharply for this typical wavelength λ_0 only. A stop at the place of this image permits the passage of a fairly narrow wavelength interval with λ_0 as its optical center of gravity. By varying the composition of a mixed liquid as Christiansen suggested, or by varying the temperature of a single liquid as I preferred, any wavelength range desired can be separated by the exit diaphragm and used for experiments.

The whole arrangement has the property of a monochromator, and as in every monochromator the purification of the light from a source emitting a continuous spectrum becomes better as the aperture of the lens and its focal length increase and worse as the areas of the entrance and exit diaphragms are increased.

The use of the device is especially desirable for such experiments as need an intense illumination over a large area with light of a narrow spectral range where intense spectral lines are not available. It has the advantage of cheapness because simple lenses of large aperture and long focus are inexpensive. Another advantage over ordinary monochromators, particularly in studying the effect of light on biological objects, is the fact that the shapes of the entrance and exit diaphragms are not limited to slits. One can give them any shape which is suitable for the object under study, e.g., with the outline of a leaf if experiments on photosynthesis are carried out.

The purity of the light emerging from the exit diaphragm depends solely on the actual arrangement and on the precision required for the experiments. Therefore, the transmission curves published by authors[2,3] who have described dispersion filters have no general meaning and are of no great use for a special case.

The purity of the light passed by the filter can be tested by any spectrophotometer. But, as the dispersion filter arrangement itself is very bulky — it can exceed lengths of 4-8 meters — and as many spectrophotometers themselves are large instruments, a simple method of

calibration appeared desirable. The simplicity of course, brings in a certain lack of precision.

I found the following device suitable (Fig. 1). The purified light emerging from the exit stop illuminates directly one-
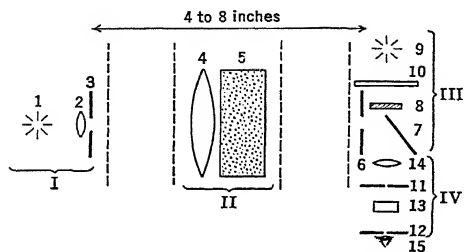
FIG. 1. Diagram of the Device. I. 1) Main light source, 2) Condenser, 3) Entrance diaphragm of Dispersion Filter. II. 4) Larger Aperature Lens, 5) Trough Filled with Glass Powder and Liquid of Dispersion Filter. III. 6) Exit Diaphragm of Dispersion Filter, 7) White Reflecting Surface as Part of Comparison Field, 8) DIN-Step-Wedge as Part of Comparison Field, 9) Auxiliary Light Source and 10) Opal Glass for Illuminating the Step Wedge. IV. 11, 12, 13) Entrance and Exit Slits and Prism of Monochromator, 14) Lens for focusing the Sharp Edge of 7 to be Viewed Sharply by the Observer 15.

half of the photometric comparison field which was placed at the same position as the object under study. It was an oblique, white surface — for instance, a sheet of white cardboard with a sharp edge. The edge could be focused by means of an auxiliary lens in the field of view of a simple monochromator with fixed angle and adjustable wavelength drum. The direct-vision monochromator after Bechstein, made by Schmidt and Haensch in Berlin, was a suitable instrument.

The matching was made by means of a normal DIN-step-wedge, with steps of $D = 0.1$, which was illuminated from behind by a lamp of the same color temperature as the lamp used for the experiments, diffused by an opal glass. The wedge

could be shifted up and down by a rack and pinion.

The reflecting plane and beside it the steps with the corresponding figures appear monochromatically in the field of view, and the matching step can be found easily by shifting the wedge.

It is best in all actual cases to search at first for the wavelength of maximum transparency by altering simultaneously the wavelength and the wedge. After having done this one lifts the wedge by three steps and searches for both wavelengths to match the field. This gives the half width of the purified light. A second reading is made after having lifted the wedge by seven more steps to find the tenth width of the light purity.

Fig. 2 shows, for three wavelengths, the purity for three different apertures of the diaphragm.
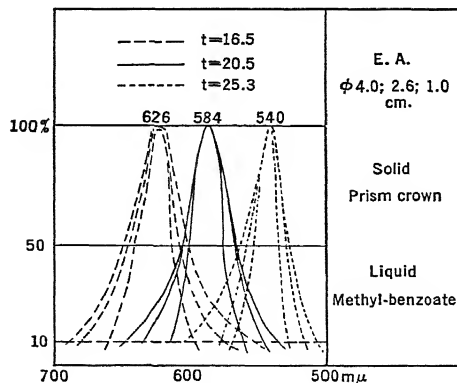
FIG. 2

REFERENCES

1. C. CHRISTIANSEN, Ann. Physik und Chemie, 23, 298 (1884); 24, 439 (1885).

2. F. WEIGERT and H. STAUDE, Z. physik. Chem., 130, 607 (1927); E. ELVEGÅRD, H. STAUDE, and F. WEIGERT, ibid (B), 2, 149 (1929).

3. K. VON FRAGSTEIN, Ann. Physik, (5) 17, 22 (1933); E. D. McALLISTER, Smithsonian Misc. Coll., 93, No. 7 (1935); H. S. DENMARK and W. M. CADY, J. Optical Soc. Am., 25, 330 (1935).

A BIBLIOGRAPHY OF SPECTROCHEMICAL ANALYSIS
1920-1937

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National Bureau of Standards

ABSTRACT

Although the possibility of recognizing chemical substances spectroscopically was mentioned 100 years ago, the methods were not highly developed or commonly applied until recent times. In fact, most of the progress in these directions has been made in the past dozen years, which thus mark a new era in the history of applied science. In this period many hundreds of papers and booklets dealing with chemical analysis by means of atomic emission spectra were published at an accelerated rate, the papers appearing in many different languages and journals, describing an amazing variety of applications to sciences and industries. The production of such a profusion of publications on applied spectroscopy was due in part to its purely empirical development, which resulted in an excessive variety of methods, light sources, electric circuits, spectrographs, photographic materials and calibrations, choices of spectral lines for identification and for quantitative determinations, etc. In spite of some impractical suggestions and notwithstanding certain limitations, spectral analysis has already displaced gravimetric analysis in many instances of routine or control work, has opened new fields in science and industry, and gives promise of going still further. The rapid growth of literature on chemical analysis with atomic spectra is shown graphically in Fig. 1, where the total output of such papers since 1920 is plotted with crosses, and the annual output with circles on right-hand ordinates of five times greater scale.
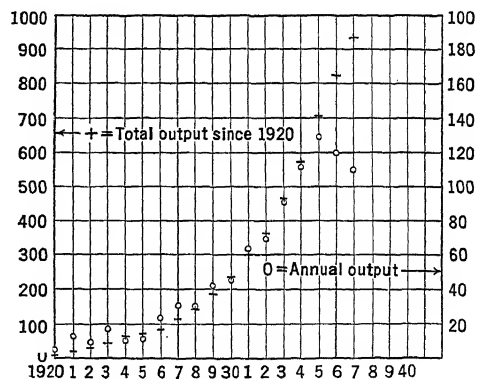
FIG. 1

The present and future workers in this field are unable to profit by the experiences of others unless they can find the widely scattered literature. To facilitate this, a number of reviews and limited bibliographies[1] have recently appeared, but no general catalog or comprehensive index of spectrochemical literature has been published.

Such a catalog, however, has been main-

tained for information purposes by the spectroscopy section of the National Bureau of Standards during the past quarter century. When this catalog was brought to the attention of the American Society for Testing Materials Committee E-2 on spectrographic analysis, a suggestion that it be made generally available resulted in a recommendation that it be published by the Society. For this purpose, 956 items in this catalog from 1920 to 1937, inclusive, were arranged in chronological order, and in alphabetical author order in each calender year. Instead of printing an abstract of each paper, references to already published abstracts are given. A large majority of these papers have been listed and abstracted in *Chemical Abstracts,* but some additional ones were found in *Biological Abstracts,* in *Mineralogical Abstracts,* and in *Science Abstracts.*

Finally, each publication listed in this bibliography was given a serial number for use in a detailed index. The content rather than the title of a paper was used in preparing this index so that the literature pertaining to any particular applica-tion, determination, instrument, method, or closely related topic can readily be found and, in addition, abstracts of the same. An effort was made to distinguish all quantitative analyses with *Chemical Abstracts* abbreviations " detn." or " quant."

The compilers attempted to include all the literature which came to their attention, but it will be obvious that not all papers listed are of equal quality. We trust that this bibliography and index will make it easier for all practical spectro-chemists to determine what, if anything, has been done on any particular problem, and where to look for desired information. For such service and benefits we are all indebted to the American Society for Testing Materials which undertook the publication and distribution of this index.

REFERENCES

1. D. M. SMITH, " Bibliography of Literature on Spectrum Analysis " (195 books and papers of Metallurgical interest). British Non-Ferrous Metals Research Association, 1935. F. TWY-MAN, " Spectrochemical Abstracts, 1933–1937 " (228 papers). Adam Hilger, Ltd. 1938.

STANDARD WAVELENGTHS

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The oldest living spectroscopists can recall the time when the fourth figure of numbers representing the wavelengths of atomic radiations was uncertain, but modern spectral data are expressed by seven or even by eight significant figures with guarantees that errors do not exceed one or two units in the last place. This increased precision is due to the invention of interferometers and refinement of new methods of measurement, and to improved control of spectra. However, relatively few spectra have been measured with the greatest possible accuracy or described completely enough for present needs, which may be enumerated as (1) unambiguous identification with chemical elements or compounds of all lines observed in laboratory or in celestial sources; (2) term analyses of spectra leading to information about atomic or molecular structure; and (3) calculations, from spectral terms, of unobserved and of forbidden lines, and of theoretical standards. For such a program it is desirable to have uniformly satisfactory standards distributed throughout the entire range of observed spectra so that wavelengths in any region may be derived from adjacent standards by interpolation. This ideal is not yet attained, but is met in part by the values adopted by the International Astronomical Union during the past ten years. Since the facts have appeared only in the *Transactions* of the Union (rarely referred to by physicists, and possibly never seen by chemists), and because all spectrochemists actually depend implicitly on these standards for the reliability of spectral data they use, I am persuaded to give a brief report on the present status of standard wavelengths.

The names Fraunhofer, Ångström, Kayser, and Rowland are associated with earlier individual efforts to set up systems of standard wavelengths for spectroscopic measurements. But even the best of these was later displaced by systems resulting from international cooperation beginning in 1904 when the question of standard wavelengths was discussed at the first meeting of the International Union for Cooperation in Solar Research. Ten years later this organization was destroyed by the World War, but its work was subsequently assumed by the International Astronomical Union organized in 1919 and now adhered to by 27 nations. A committee on standard wavelengths and solar spectrum tables has made recommendations which have been adopted by the Union from time to time, thus creating the present system of international standards, consisting of (1) a primary standard, (2) secondary standards from the spectrum of the iron arc, (3) tertiary or interpolated

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iron standards, (4) secondary standards from noble-gas spectra, and (5) solar-spectrum standards.

(1) The primary standard is based on the interferometer measurement of the wavelength of the red radiation from cadmium vapor in terms of the international meter bar (as reported by Benoit, Fabry, and Perot in 1907). It is defined as follows: " The wavelength of the red ray of light from cadmuim produced by a tube with electrodes is 6438.4696 angstroms in dry air at 15° C on the hydrogen thermometer, at a pressure of 760 mm of mercury the value of g being 980.67 (45°)." Specifications for the operating conditions of the light source have been adopted by the International Committee on Weights and Measures and by the International Astronomical Union.

(2) Secondary standards represent the mean of three independent, concordant measurements of wavelengths of selected lines from sources under specified operating conditions, the wavelength measurements being made relative to the primary standard by the interferometer method devised by Fabry and Buisson in 1907. The source for iron lines is specified as " the Pfund arc operated between 110 and 250 volts, with 5 amperes or less, at a length of 12-15 millimeters used over a central zone at right angles to the axis of the arc, not to exceed 1-1.5 millimeters in width, and with an iron rod 6-7 millimeters diameter as the upper pole and a bead of oxide of iron as the lower pole." Since the secondary standards of iron are indispensable for accurate spectroscopic measurements, but are to be found only in various volumes of *Transactions of the International Astronomical Union,* a complete list is made available here in Table I. Preliminary values of infrared iron lines (7164.469 to 10216.351 A) and of additional ultraviolet ones (2100.794 to 3383.980 A) may be found in the *Bureau of Standards Journal of Research,* 14, 33 (1935); 18, 543 (1937).

(3) Tertiary standards, derived by grating or interferometer interpolation between secondaries, are given for 312 iron lines (3370.787 to 6750.156 A) in *Transactions of the International Astronomical Union,* 3, 86 (1928).

(4) Owing to the high homogeneity and remarkable reproducibility of certain lines characteristic of noble gases it appears that a higher order of accuracy is possible in the determination of these wavelengths relative to the primary standard or relative to one another. The I.A.U. has adopted values for neon and krypton lines quoted in Tables II and III respectively. These standards are frequently used for testing precision end-gauges, ruled scales, etc.

(5) Solar-spectrum standards, also measured interferometrically, have been adopted in the spectral ranges 3592.027 to 7122.206 A and 7568.906 to 9889.050 A, but since these are primarily of interest to astrophysicists rather than to mundane spectrochemists the quotation of further details from the *Transactions of the International Astronomical Union* could not be justified here.

In conclusion, it should be emphasized that the range of spectrum covered by secondary standards is still relatively small and needs extension especially in the infrared and in the ultraviolet. Laboratories possessing suitable equipment and an observer temperamentally inclined toward precision measurements are urged to co-operate in the production of further wavelength standards, the fundamental importance of which is abundantly attested by modern applications to metrology, astrophysics, and chemical analyses in scientific and industrial laboratories.

TABLE I

IRON ARC SECONDARY STANDARDS OF WAVELENGTH, MEASURED IN AIR AT 15° C
AND 760 MM PRESSURE, IN A.

2447.708	3184.896	3585.320	3799.549	3966.066	4337.049	4741.533	5341.026
2584.536	3191.659	3586.114	3805.345	3967.423	4352.737	4745.806	5371.493
2635.808	3196.930	3589.107	3815.842	3969.261	4358.505	4772.817	5397.131
2679.062	3200.475	3608.861	3824.444	4005.246	4369.774	4786.810	5405.778
2689.212	3205.400	3617.788	3825.884	4014.534	4375.932	4789.654	5429.699
2699.107	3215.940	3618.769	3827.825	4045.815	4383.547	4859.748	5434.527
2723.577	3217.380	3621.463	3834.225	4063.597	4390.954	4878.218	5446.920
2735.475	3222.069	3631.464	3839.259	4066.979	4404.752	4903.317	5455.613
2767.523	3225.789	3647.844	3840.439	4067.275	4408.419	4918.999	5497.519
2778.221	3236.223	3649.508	3841.051	4071.740	4415.125	4924.776	5501.469
2804.521	3239.436	3651.469	3843.259	4107.492	4422.570	4939.690	5506.782
2813.288	3244.190	3669.523	3846.803	4114.449	4427.312	4966.096	5569.625
2823.276	3257.594	3676.314	3849.969	4118.549	4430.618	4994.133	5572.849
2832.436	3271.002	3677.630	3850.820	4121.806	4442.343	5001.871	5586.763
2838.120	3284.588	3679.915	3856.373	4127.612	4443.197	5012.071	5615.652
2851.798	3286.755	3687.458	3859.913	4132.060	4447.722	5041.759	5624.549
2869.308	3298.133	3695.054	3865.526	4134.681	4454.383	5049.825	5658.826
2912.158	3340.566	3704.463	3867.219	4143.871	4459.121	5051.636	5662.525
2929.008	3347.927	3705.567	3872.504	4147.673	4461.654	5083.342	6027.057
2941.343	3370.786	3719.935	3873.763	4156.803	4466.554	5110.414	6065.487
2953.940	3396.978	3722.564	3878.021	4170.906	4489.741	5123.723	6136.620
2957.365	3399.336	3724.380	3878.575	4175.640	4494.568	5127.363	6137.696
2965.255	3401.521	3727.621	3886.284	4184.895	4517.530	5150.843	6191.562
2981.446	3407.461	3732.399	3887.051	4202.031	4528.619	5167.491	6230.728
2987.292	3413.135	3733.319	3888.517	4203.987	4531.152	5168.901	6252.561
2999.512	3427.121	3734.867	3895.658	4213.650	4547.851	5171.599	6265.140
3037.388	3443.878	3737.133	3899.709	4216.186	4592.655	5198.714	6318.022
3047.605	3445.151	3738.308	3902.948	4219.364	4602.944	5202.339	6335.335
3057.446	3465.863	3748.264	3906.482	4250.790	4647.437	5216.278	6393.605
3059.086	3476.704	3749.487	3907.937	4260.479	4667.459	5227.192	6421.355
3067.244	3485.342	3758.235	3917.185	4267.830	4678.852	5242.495	6430.851
3075.721	3490.575	3760.052	3920.260	4271.764	4691.414	5250.650	6494.985
3083.742	3497.843	3763.790	3922.914	4282.406	4707.281	5270.360	6546.245
3091.578	3513.820	3765.542	3927.922	4285.445	4710.286	5307.365	6592.919
3116.633	3521.264	3767.194	3930.299	4294.128	4733.596	5328.534	6663.446
3134.111	3558.518	3787.883	3935.815	4298.040	....	....	6677.993
3157.040	3565.381	3790.095	3940.882	4305.455	....	....	....
3160.658	3576.760	3795.004	3942.443	4307.906	....	....	....
3175.447	3581.195	3797.517	3948.779	4315.087	....	....	....
3178.015	3584.663	3798.513	3956.681	4325.765	....	....	....

TABLE II		TABLE III	
Neon Secondary Standards of Wavelength, Measured in Air at 15° C and 760 mm Pressure		Krypton Secondary Standard Wavelengths, Measured in Air at 15° C and 760 mm Pressure	
5852.4878	6266.4950	4273.9700	4453.9179
5881.8950	6304.7892	4282.9683	4463.6902
5944.8342	6334.4279	4286.4873	4502.3547
5975.5340	6382.9914	4300.4877	5562.2257
6029.9971	6506.5279	4318.5525	5570.2895
6074.3377	6532.8824	4319.5797	5649.5628
6096.1630	6598.9529	4351.3607	5870.9158
6143.0623	6678.2764	4362.6423	5993.8503
6163.5939	6717.0428	4376.1220	6421.029
6217.2813	7032.4127	4399.9670	6456.291

NEW TABLES OF THE 100,000 PRINCIPAL SPECTRUM LINES OF THE CHEMICAL ELEMENTS BETWEEN 10,000 A and 2000 A

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The most recent systematic surveys of the spectrum lines of a large number of the elements made on a consistent basis were completed more than 25 years ago,[1] and tables compiled from measurements scattered through the literature are now far from complete. New tables which would list many more lines appear to be needed, these lines to be measured with greater and more uniform precision, and with intensities on a more expanded scale.

In this laboratory we have recently completed two catalogs of all the atomic lines, measurements on which have been reported in the literature. Data for a line were listed on each of 250,000 white cards by one set of workers. Independently, another set of workers made a second catalog direct from the literature, data for a line being listed on each of 250,000 buff cards. Buff and white catalogs were then intercompared and mutually corrected. The white cards were then arranged in order of wavelengths under each element; the buff cards were arranged in order of wavelengths for all elements.

Numerous inconsistencies were found in the literature values, as might be expected when so large a number of workers is responsible for the data and such a wide variety of methods is used. It was decided that data for inclusion in any projected new tables were of sufficient importance to justify new measurements.

Systematic remeasurement of all spectrum lines is of course a tremendously detailed task. Kayser's monumental " Handbuch der Spektroscopie " lists a total of some 120,000 different lines, and the catalogs prepared from the literature during the present work will contain more than 200,-000 lines after elimination of all apparent duplicates. We have made more than ten thousand 20-inch spectrograms with gratings of higher resolution, greater dispersion, and more efficient light control than have previously been used for wavelength measurements, and find that the number of lines to be included in useful tables might well approach one million, if all lines emitted between 50,000 A and 100 A by all atoms in their first five stages of ionization were included. We find that such elements as iron and cerium, after impurity and other false lines have been eliminated, emit at least four times as many important lines as are listed in the literature.[2] Though such extensions of data are of relatively little value for spectrochemical analysis, they are of great importance to the spectroscopist who wishes to set up quadratic arrays and term diagrams as preliminaries to atomic-structure determinations. It seems perfectly safe to say that the necessary examination of atomic spectra is less than one-fourth complete.

It was therefore considered to be worth while to launch a project for the collection

of further wavelength data. Since more than twenty million individual measurements would be required, some method of plate measurement and reduction was needed which would be more rapid than the usual hand comparator and electrical calculating machine, so a new type of automatic comparator was constructed.[3] Assistance of the Works Progress Administration was obtained in furnishing clerical help and materials, and a wavelength project was begun which has now been in operation for three years. More than ten million measurements have thus far been made, and checks on some of the results indicate that final wave-number values are correct on the average to within ± 0.03 cm⁻¹. Wavelengths in the shorter regions can be trusted to a few thousandths of an angstrom (in the cases tested, to within ± 0.0018 A for more than 60 per cent of the lines,[2] and in the longer regions to ± 0.01 A, unless the lines are unusually broad.

Issuance of complete tables is considered inadvisable until measurements for all atoms have been checked by means of the correspondence principle, and since this work must be carried out by research spectroscopists it will require a number of years. Tables appear to be badly needed, however, which would contain the 100,000 lines most strongly emitted between 10,000 and 2000 A by the chemical elements under normal conditions of excitation, arranged for purposes of spectrochemical analysis in order of wavelengths without segregation under elements. Since the tables in this form would also be useful to spectroscopists, at least until more complete tables segregating the lines by elements can be compiled, it seemed desirable also to include wave numbers.

Publication of such analytical tables is now being undertaken, but owing to the great cost of manufacture this must be

delayed until assurance is obtained of sufficient demand to pay for printing of the tables. Pre-publication subscriptions have therefore been solicited at $12 per copy net, the necessary post-publication price probably being $18 or more. A sample of tabular material is shown in Table I.* The 350 pages of size about 8½ by 11 inches will include 334 pages each containing data on 300 lines, a few pages of short tables con-

TABLE I

Wave-length	El	Intensities			R	Wave-number
		A	S	D		
3007.879	Cb	2h	—	—	C	33236.36
3007.739	NdII	—	100	—	C	33237.91
3007.629	Mo	500R	—	—	—	33239.12
3007.477	Cb	2	—	—	C	33240.80
3007.286	Cb	1	2	—	C	33242.91
3006.559	NdII	—	8	—	C	33250.95
3006.150	Sm	30	20	—	—	33255.48
3006.037	NdII	—	4	—	AC	33256.72
3005.222	Ir	20	—	—	—	33265.74
3005.155	NdII	—	1	—	C	33266.49
3005.083	Gd	1	1	—	—	33267.29
3005.009	Mo	—	2	—	—	33268.10
3004.914	Sm	6	—	—	—	33269.15
3003.579	Gd	1	1	—	—	33283.94
3003.338	U	1	2	—	—	33286.61
3003.222	NdII	—	3	—	C	33287.90
3003.219	Cb	2	1	—	—	33287.93
3002.882	Gd	2	1	—	—	33291.66
3002.728	Ti	3	—	—	—	33293.37
3002.489	NdII	—	4	—	C	33296.02
3002.508	Ir	3	2	—	A	33295.82
3002.48	KrII	—	1	1	C	33296.12
3000.870	Ti	20	10	—	SC	33313.99
3000.788	U	1	2	—	—	33314.90
3000.511	NdII	—	3	—	C	33318.97
3000.243	Mo	4	—	—	A	33320.95
3000.119	Cb	7h	—	—	—	33322.32
3000.094	U	1	2	—	—	33322.60
3000.030	NdII	—	3	—	C	33323.31
3000.029	Ir	1	1	—	A	33323.32

taining lists of sensitive lines of the elements, and a few pages of descriptive material interpreting the tables and telling how the measurements were made. Publication of the tables will be undertaken as soon as 500 copies are subscribed for, payment being required only on delivery of the volume.

Approximately 75 per cent of the data included will consist of new material obtained in the present project. To avoid

*This material is merely illustrative and is far from complete even for the range given.

TABLE II

APPROXIMATE NUMBERS OF LINES TO BE INCLUDED UNDER EACH ELEMENT
(10,000 to 2000 A only)

Atomic Number	Element	Number of Lines	Atomic Number	Element	Number of Lines
1	Hydrogen	22	47	Silver	1348
2	Helium	160	48	Cadmium	1386
3	Lithium	72	49	Indium	1241
4	Beryllium	104	50	Tin	327
5	Boron	168	51	Antimony	1014
6	Carbon	166	52	Tellurium	1175
7	Nitrogen	470	53	Iodine	1103
8	Oxygen	226	54	Xenon	1068
9	Fluorine	318	55	Cesium	1720
10	Neon	633	56	Barium	729
11	Sodium	439	57	Lanthanum	1786
12	Magnesium	217	58	Cerium	3000
13	Aluminum	525	59	Praseodymium	1539
14	Silicon	561	60	Neodymium	2442
15	Phosphorus	600	61	Illinium	. . . .
16	Sulfur	473	62	Samarium	3000
17	Chlorine	832	63	Europium	3000
18	Argon	1285	64	Gadolinium	2118
19	Potassium	449	65	Terbium	2706
20	Calcium	1483	66	Dysprosium	2782
21	Scandium	980	67	Holmium	841
22	Titanium	3000	68	Erbium	1962
23	Vanadium	3000	69	Thulium	548
24	Chromium	1824	70	Ytterbium	2046
25	Manganese	1269	71	Lutecium	708
26	Iron	6000	72	Hafnium	2331
27	Cobalt	3000	73	Tantalum	2366
28	Nickel	1430	74	Tungsten	2216
29	Copper	1889	75	Rhenium	1963
30	Zinc	726	76	Osmium	926
31	Gallium	270	77	Iridium	2538
32	Germanium	219	78	Platinum	733
33	Arsenic	412	79	Gold	461
34	Selenium	902	80	Mercury	1537
35	Bromine	401	81	Thallium	426
36	Krypton	1870	82	Lead	684
37	Rubidium	927	83	Bismuth	688
38	Strontium	237	84	Polonium	. . . .
39	Yttrium	1573	85	. . . .	. . . .
40	Zirconium	2948	86	Radon	412
41	Columbium	3000	87	. . . .	. . . .
42	Molybdenum	2665	88	Radium	234
43	Masurium	. . . .	89	Actinium	. . . .
44	Ruthenium	2002	90	Thorium	3000
45	Rhodium	1229	91	Protoactinium	. . . .
46	Palladium	1029	92	Uranium	1103

delaying publication of the tables until all measurements are complete, it has been decided to include for certain elements some data taken from the literature. Values so obtained are being critically chosen, and those responsible for the measurements used are being credited with them.

The approximate numbers of lines to be included under each element are given in Table II. In general all lines of intensity greater than 1 on an expanded scale are included, but this is of course a very loose criterion. Some elements have been more carefully studied than others, and intensities depend on a great many factors. A sufficiency of lines are included in the tables, however, to insure that probably few important lines which appear in the arc, spark, or discharge tube have been omitted.

Elements for which no lines are recorded in Table II are those for which we have been unable to obtain material. We respectfully bring this lack to the attention of chemists, especially of those responsible for naming elements 43, 61, 85, and 87.

Wavelengths are given in the tables to seven figures if shorter than 6800 A, and to six figures if longer. Wave numbers are given to seven figures throughout the tables. Intensities are given on a scale of 10,000 to 2, lines of intensity 1 or 0 being omitted.

For taking the spectrograms, three aluminum-on-glass concave gratings of 6-inch aperture ruled by Professor R. W. Wood at the Johns Hopkins University were used. These gratings are of 35-foot radius of curvature, one having 15,000 and two 30,000 lines per inch. Most of the spectrograms taken had dispersions of 0.4 A per millimeter if in the range 2000 to 4500 A, 0.8 A per millimeter if betweeen 4500 and 6800 A, and 3.3 A per millimeter if between 6800 and 10,000 A. Eastman plates were used, of type I-O and of various other types sensitized for the various regions of the visible and infrared regions. Exposures ranged from a few seconds to 10 hours. The international iron arc was used for wavelength standards, and at all wavelengths shorter than 4500 A a long arc of the Pfund type was used in exciting the various atoms to emit light. When photographing longer wavelengths the arc was shortened to bring out greater numbers of lines. The spark was of the standard condensed type. Discharge tubes were of the quartz capillary type.

After the automatic comparator had been in use night and day for two years it became badly worn. An improved model had been built in the meantime,[4] and when this had been put into successful operation the original model was completely rebuilt and provided with a 27-inch screw like that of the second machine, instead of its original 16-inch screw. This instrument, photographed while in course of construction and before its electrical controls and protective case were installed, is shown in Fig. 1. In this improved model an electron multiplier tube is used instead of photocells and a-c amplification, giving greatly increased sensitivity and steadiness. The densitometer trace is now made with a cathode-ray oscillograph. At present an improved form of maximum-density picker using an all-electric method of line setting is being installed.

In order that too much weight should not be given to measurements made by the automatic method, all measurements have been duplicated by hand operation, the machine merely calculating and recording the wavelengths. The operator sets on the lines, pressing a key when in his judgment the instrument is properly set. This method, though considerably slower than automatic operation, is yet 20 times as fast as ordinary hand methods.

The greatest source of error in the measurements appears to arise from the wavelength standards. The International secondary standards of iron appear to have been chosen because of their great intensities, this facilitating interferometer measurements. In order to get a sufficient number of intermediate iron standards, however, it was necessary to expose so

cerium lines will be measured with Fabry-Perot interferometers, but it is thought inadvisable to hold up the present tables until this can be completed, since the average precision is now probably at least treble that of most tables available for spectrochemical purposes.

Lines whose wavelengths are particularly trustworthy are designated in the tables

FIG. 1

heavily to the iron arc that the secondary standard lines are greatly broadened. The tertiary standards appear to have lower precision than most of our measurements, and our scale can be considerably improved when more suitable standards are available. It is our present plan ultimately to use cerium lines as standards, since these are well distributed, even in intensity, and easy to produce. The

with the letter A; internationally accepted standards are marked S; and lines whose wave numbers have been checked by the selection principle are designated C. Lines whose wave numbers are calculated from theory, but whose wavelengths have been measured, are marked c.

The intensity values published with most wavelength tables are very rough eye estimates, but these are usually quite

meaningful within a given element. More exact intensity measurements have little meaning unless plate sensitivity, excitation conditions in the source, and numerous other factors are controlled. Eye estimates made by different observers vary greatly, however, and in the present case all intensities have been made on a scale which is fairly uniform.

The intensity scale was calibrated by making eye estimates in the usual manner on a typical plate, and at the same time
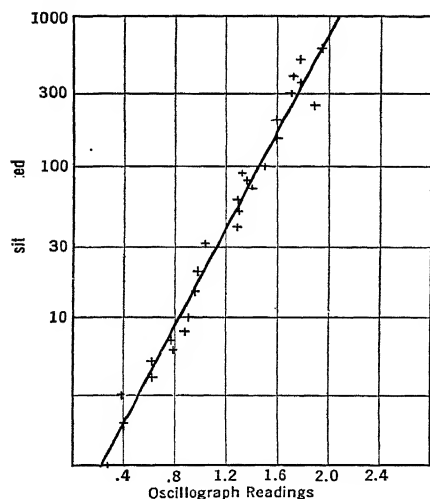
FIG. 2

measuring densities photoelectrically. The response of the galvanometer was then calibrated in terms of the eye estimates, as shown in Fig. 2. It is observed that a fairly straight line is obtained if log I_{eye} is plotted against galvanometer deflection.

Measurements made by persons unfamiliar with the background of their work must, of course, be carefully checked. Final checking is being carried out by graduate student spectroscopists who are setting on the lines of the best set of plates for each element, and, with a card catalog

of previous measurements at one elbow and a clerk to record remarks at the other, are passing final judgment on each line in turn. As each line is identified its intensity is recorded, and possible masking and ghost lines are taken account of.

Such a project depends for its successful completion in a reasonable time on the cooperation of many individuals. Among those who have been most responsible for the present work are the following:

For the organization and supervision of the non-scientific aspects of the project, Colonel Robert C. Eddy of the Massachusetts Institute of Technology.

As supervisors in various phases of the project at different times: Dr. Richard Evans, Dr. Fred W. Paul, Dr. Peter A. Cole, Dr. Joseph Morgan, John D'Albora, Simeon Rosenthal, Henry Rich, Leonard Julian, William W. Bartlett, Julius Molnar, Dr. Harriet Allen.

Skillful technical help by Walter H. Kallenbach, Carl G. Selig, and Norman Oliver and their assistants has contributed much to mechanical aspects of the undertaking. Checking of certain elements was greatly expedited by Professor Walter E. Albertson of the Massachusetts Institute of Technology and Professsor Dorothy W. Weeks of Wilson College.

The great burden of numerical tabulation and checking has rested on a very faithful group of W. P. A. workers. They cannot be mentioned individually because of numbers, but it is a pleasure to record that the project would have been impossible without their conscientious work.

Scientific staff, housing, apparatus, and financial support for the project were furnished by the Massachusetts Institute of Technology; clerical help, some technical help, and a considerable amount of materials were furnished by the Works Progress Administration for Massachusetts

under Projects 165-14-6999-0 and 465-14-3-149. Pure chemicals for production of spectra were purchased with several grants from the Rumford ·Fund of the American Academy of Arts and Sciences, which are gratefully acknowledged.

Note added in proof: Publication of the tables described above has now been assured. Owing to the opinion expressed by a number of spectroscopists that wave numbers are unnecessary in tables designed primarily for spectrochemical analysis, it has been decided to omit these. A somewhat cheaper and less bulky volume will result, or the number of wavelengths included may be increased to 120,000. At the present writing the tables are undergoing final arrangement for the printer.

REFERENCES

1. EXNER and HASCHEK, "Die Spektren der Elemente bei normalem Druck," F. Deuticke, Wien, 1911; EDER and VALENTA, "Atlas typischer Spektren," A. Hölder, Wien, 1911, 1928.
2. HARRISON and ALBERTSON, *Phys. Rev.*, 53, 940 (A) (1938); WEEKS and HARRISON, *ibid.*, 54, 312 (A) (1938).
3. G. R. HARRISON, *J. Optical Soc. Am.*, 25, 169 (1935).
4. G. R. HARRISON, *Rev. Sci. Instruments*, 9, 15 (1938).

THE APPLICATION OF SPECTROGRAPHIC METHODS TO THE DETERMINATION OF TOTAL BODY WATER WITH SULFANILAMIDE

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From a functional point of view it may be considered that the water in the body is distributed in three compartments: (1) blood plasma; (2) interstitial fluid; and (3) intracellular fluid. The volume of the blood plasma has been determined by a variety of dilution methods. Most successful have been the dye methods, and in recent years, determinations of the dyes with spectrophotometric technique have increased their accuracy. There is now evidence that the fluid available for the dilution of sodium thiocyanate is approximately equal to that of the interstitial fluid plus the blood plasma. Hence, by combining the thiocyanate method with the dye method one can measure, at least approximately, the volume of the interstitial compartment. If it were possible to measure total body water, and simultaneously to determine the fluid available for the solution of thiocyanate, one could also estimate the amount of water in the third and largest compartment, namely, the intracellular.

Of prime interest, then, is the development of a dilution method for estimating total water in the unanesthetized animal and in man. Hitherto, this was possible only by drying the tissues after sacrificing the animal. The substance used in the dilution method must be non-toxic and preferably pharmacologically inert; it must be distributed in the same concentration in the water of all the tissues, but must not shift the water in the different fluid compartments.

Data in the literature on urea and on its distribution in the animal body normally and after injection indicate that this substance should be suitable for the determination of total body water in animals in the normal state of water balance.[1,2] However, the metabolism of urea is altered when the water balance is disturbed. Therefore, it would be more desirable to find a substance that is entirely foreign to the body. A number of possibilities were investigated, and, for several reasons, sulfanilamide was selected. In a study of the distribution of this substance in the dog, it appears that the concentration of sulfanilamide is the same for all tissues on the basis of water content.[3] Thus, it should be possible to determine total water by measuring the extent to which a known amount of the substance, injected into the blood, is diluted in the body fluids. One difficulty is encountered, namely, that some time is required for uniform distribution. Also, while this occurs, the substance is being excreted by the kidneys, and one must know how much is lost during the period of diffusion. The necessary in-

formation may be obtained from a careful study of the time-concentration curve of the substance in the blood stream and from an analysis of the urine.

The substances which are used to determine total water must be compounds for which quantitative methods of analysis in blood and urine are available. It will be seen that there are difficulties here which can be satisfactorily overcome by applying spectrographic methods. The urea determinations were made with the Van Slyke manometric-gasometric method. For most of the sulfanilamide experiments the procedure of Marshall, Emerson, and Cutting[4] was employed, except that the Königs-Marten spectrophotometer was used instead of a colorimeter. This method has great advantages: it (1) eliminates the preparation of standards, (2) permits analyses of small samples (0.5 cc or less), and (3) increases accuracy. The unknowns were read against a blank prepared from the blood withdrawn before the injection. All readings were made at 5300 A° which is the peak of absorption for the red azo dye obtained upon diazotizing and coupling sulfanilamide with dimethyl-α-naphthylamine (see Fig. 1). It was found that sulfanilamide in concentrations from 1.0 to 15.0 mg per cent solution could be completely recovered from water, serum, and whole blood.[5] These spectrophotometric results demonstrate also that the intensity of color developed is directly proportional to the concentration of sulfanilamide in the original solutions.

The time-concentration curves of blood in the urea and sulfanilamide experiments indicate that distribution of both substances is complete approximately 1 hour after intravenous injection. Beyond this period the disappearance rates of the compounds are practically constant for several hours.[6] Linear extrapolation of

this portion of the curve gives the original concentration which would be obtained if distribution were complete and none of the substance had been excreted. Calculations based on this assumption show that the two substances are distributed in approximately the same volume. In the dog, the values for "available water"[6] agree closely with the total water determined by desiccation.[7,8,9,10]

Gregersen and Stewart[11] have demonstrated that determinations of plasma volume with the dye T-1824[12] can be combined
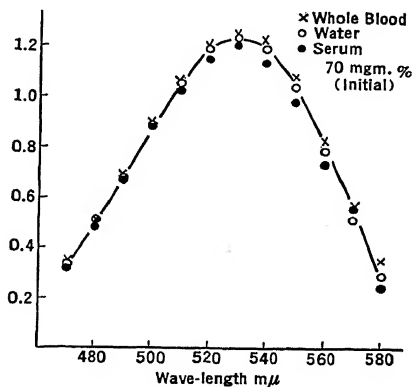
FIG. 1. Spectral Absorption Curve of Red Azo Dye.

with the thiocyanate dilution method.[13] It has been shown recently that these two methods can be carried out simultaneously with the sulfanilamide determinations, provided that the latter are done spectrographically.[5] The original chemical procedure was not satisfactory, because the thiocyanate in the blood interfered with the coupling of dimethyl-α-naphthylamine with sulfanilamide. It was found that sulfanilamide in water solution and in blood (alcoholic extract) shows a single broad band in the region 2300 A° to 2900 A°, with maximal absorption at 2590 A°. The ab-

sorption curves of two aqueous solutions appear in Fig. 2. When thiocyanate is added to the solutions in the concentration
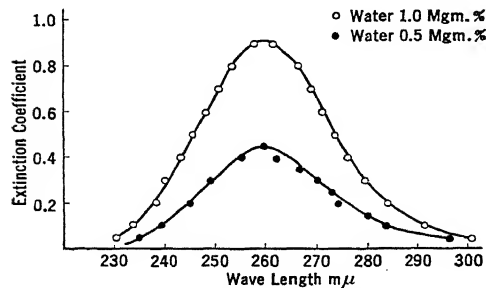
FIG. 2. Spectral Absorption Curve of Sulfanilamide.

which is found in an experiment where dye and thiocyanate have been injected, there is no change in the shape or position of the curve.

The estimation of total water in man involves the analysis of sulfanilamide and
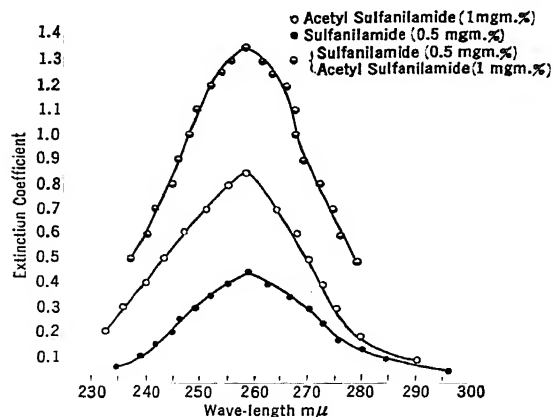
FIG. 3. Spectral Absorption Curves of Compounds in Aqueous Solution.

acetyl sulfanilamide, since a portion of the former after injection into the human body is rapidly conjugated with acetic acid. Only by spectrographic methods is it possible conveniently to determine the combined amount of these substances at any one time. Fig. 3 shows that the absorption of an aqueous solution of acetyl sulfanilamide occurs at 2580 A°. When a solution of sulfanilamide with a known extinction coefficient is added to the solution containing the conjugated form, the extinction coefficient equals the sum of the coefficients of the components within the limits of experimental error. Experiments using the acetyl sulfanilamide show distribution to be identical with that of sulfanilamide in the dog. It should be possible by using spectrographic technique to determine total body water in man.

REFERENCES

1. E. K. MARSHALL, JR., and DAVID M. DAVIS; J. Biol. Chem., 18, 53–80 (1914).
2. K. L. GAD ANDRESEN, Biochem. Z., 116, 266–302 (1921).
3. E. K. MARSHALL, JR., KENDALL EMERSON, JR., and W. C. CUTTING, J. Pharmacol., 61, 196–204 (1937).
4. E. K. MARSHALL, JR., KENDALL EMERSON, JR., and W. C. CUTTING, J. Am. Med. Assoc., 108, 953–957 (1937).
5. MAGNUS I. GREGERSEN and E. E. PAINTER, Proc. Am. Physiol. Soc., 1938.
6. E. E. PAINTER, ibid., 1938.
7. C. PH. FALCK and TH. SCHEFFER, Arch. physiol. Heilk., 13, 508–522 (1854).
8. LUDWIG PFEIFFER, Z. Biol., 23, 340–380 (1887).
9. KARL THOMAS, Arch. Anat. Physiol., Physiol. Abt., 9–38 (1911).
10. W. ENGELS, Arch. exptl. Path. Pharmakol., 51, 346–360 (1904).
11. MAGNUS I. GREGERSEN and JOHN D. STEWART, in press, 1938.
12. MAGNUS I. GREGERSEN, J. G. GIBSON, and E. A. STEAD, Am. J. Physiol., 113, 54–55 (1935).
13. LATHAN A. CRANDALL and MILFORD X. ANDERSON, Am. J. Digestive Diseases Nutrition, 1, 126–131 (1934).

THE STRUCTURE AND ABSORPTION SPECTRA OF AZO DYES

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In a continuation of studies in this field,[1] the absorption spectra of a number of mono- and di-substituted phenylazophenols have beeen observed. In the first of these papers,[2] published some ten years ago, a detailed study was made of the effect of the methyl substitution on the position and intensity of the absorption bands in three different solvents: 95 per cent alcohol, concentrated hydrochloric acid, and 3 per cent aqueous sodium hydroxide. This series was subsequently extended[3] to include a group of nitro and methylnitro substituted dyes.

Although these two series were in fair agreement with regard to the relative influence of the position of substitution on the color of the compounds, it was considered worth while to extend the series to the halogen substituted derivatives. With the completion of the series which is described in this paper it is felt that a further extension of the series is not necessary in view of the agreement between these data and those previously obtained. The results are in general in very good agreement with the predicted values which were based on these earlier data.

The new series of dyes studied are indicated in Table I. A few of these have not been reported previously in the liter-

ature and hence were analyzed in addition to the determination of the physical properties. All other samples were checked against the literature data to insure adequate purity. In all, twenty-eight compounds were studied; some twenty-four compounds have been previously reported. As far as possible the abbreviated system of nomenclature of the compound has been maintained, using o and m to indicate substitutions in the ring with the auxochromic group para to the azo, and o', m', and p' to indicate the ortho, meta, and para positions in the ring without the auxochrome. o and m indicate ortho and meta with regard to the OH group, and o', m', and p' indicate ortho, meta, and para positions in the second ring with regard to the azo group. An abbreviated tabulation of the compounds studied is given in Table II.

In the earlier studies on the methyl and nitro substituted compounds it was noted that:

1. An increase in the molecular weight shifted the absorption band towards lower frequencies, as would be predicted from other known data.

2. p' substitutions produce an increase in specific extinction over that of other substituted and unsubstituted compounds.

3. The extinction coefficients of other substituted compounds fall into a regular series, with the o-o' compounds exhibiting the lowest specific extinction.

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*The data in this paper include material abstracted from theses presented for advanced degrees under the author by L. E. Cheyney, J. R. Schaeffer, M. L. Ernsberger, and K. L. Metcalf.

4. In sodium hydroxide as a solvent there appear to be two bands of slightly different frequency values in equilibrium with each other, and this equilibrium is influenced by the positions of the substituting groups. The low-frequency component is increased by substitutions ortho to the azo group in either ring, the high-frequency component being increased by substitutions ortho to the auxochromic group, and no change in the relative intensities of the two components is produced by substitutions in the m' or p' positions. Comparison is always made with the equilibrium in the unsubstituted phenolazophenol.

The data obtained are indicated graphically in Figs. 1, 2, 3, and 4. A study of these data leads to the following generalizations:

1. An increase in molecular weight is usually accompanied by a decrease in frequency of the absorption bands. This decrease is roughly proportional to the increase in molecular weight, but varies with the position of substitution.

TABLE I

Compound	Melting Point		Abbreviation
	Experimental	Literature	
o-Chlorobenzeneazophenol	107.2°	107°	o'-Cl
m-Chlorobenzeneazophenol	134.3	135	m'-Cl
p-Chlorobenzeneazophenol	156.1	157	p'-Cl
Benzeneazo-o-chlorophenol	87.6	88	o -Cl
Benzeneazo-m-chlorophenol	114.2	115	m -Cl
o-Chlorobenzeneazo-o-chlorophenol	84.3	84	o'-Cl-o-Cl
o-Chlorobenzeneazo-m-chlorophenol	186.2	186	o'-Cl-m-Cl
m-Chlorobenzeneazo-o-chlorophenol	126.0	126	m'-Cl-o-Cl
m-Chlorobenzeneazo-m-chlorophenol	139.0	139	m'-Cl-m-Cl
p-Chlorobenzeneazo-o-chlorophenol	138.9	139	p'-Cl-o-Cl
p-Chlorobenzeneazo-m-chlorophenol	171.0	171	p'-Cl-m-Cl
o-Bromobenzeneazophenol	95.6	97	o'-Br
m-Bromobenzeneazophenol	132.5	136	m'-Br
p-Bromobenzeneazophenol	160.5	162	p'-Br
Benzeneazo-o-bromophenol	78.5	78	o -Br
Benzeneazo-m-bromophenol	127.8	128	m -Br
o-Bromobenzeneazo-o-bromophenol	119.1	119	o'-Br-o-Br
o-Bromobenzeneazo-m-bromophenol	110.2	110	o'-Br-m-Br
m-Bromobenzeneazo-o-bromophenol	155.0	155	m'-Br-o-Br
m-Bromobenzeneazo-m-bromophenol	171.5	173	m'-Br-m-Br
p-Bromobenzeneazo-o-bromophenol	142.4	143	p'-Br-o-Br
p-Bromobenzeneazo-m-bromophenol	164.9	165	p'-Br-m-Br
p-Iodobenzeneazophenol	168.0	172	p'-I
p-Bromobenzeneazo-o-chlorophenol	130.2	132	p'-Br-o-Cl
p-Nitrobenzeneazo-o-bromophenol	172.5	....	p'-NO_2-o-Br
p-Nitrobenzeneazo-o-chlorophenol	216	....	p'-NO_2-o-Cl
p-Tolueneazo-o-chlorophenol	118.6	....	p'-CH_3-o-Cl

2. Substitution in the p' position by nitro, methyl, or halogen produces a maximum in the magnitude of the absorption bands in all solvents. In alcohol, the only solvent for which complete information is available, the order of magnitude is $CH_3 < Cl < Br < I < NO_2$.

TABLE II

un*		o	m (auxochrome ring)
un*		1, 2, 3	1, 2, 3
o'	1, 2, 3, 4	1, 2, 3, 1/4†	1, 2, 3, 1/4
m'	1, 2, 3, 4	1, 2, 3, 1/4	1, 2, 3, 1/4
p'	1, 2, 3, 4, 5,	1, 2, 3, 1/2 2/3, 1/4, 2/4, 3/4	1, 2, 3, 1/4

1 = CH_3, 2 = Cl, 3 = Br, 4 = NO_2, 5 = I.
* un = unsubstituted position.
† 1/4, numerator (1) indicates CH_3 in auxochrome ring, and denominator (4) indicates NO_2 in (1) ring.

(p') ⟨ ⟩—N=N—⟨ ⟩—OH
(m') (o') (m) (o)
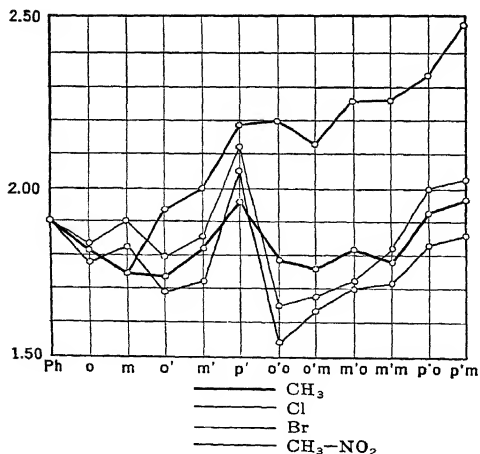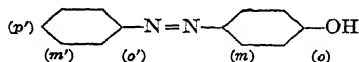
Fig. 1. Extinction Values of the Absorption Maxima of the Compounds Indicated in Alcohol.

3. Substitution of halogen atoms in the o'-o position in the disubstituted compounds produces a very marked decrease in the magnitude of the absorption bands in all solvents.
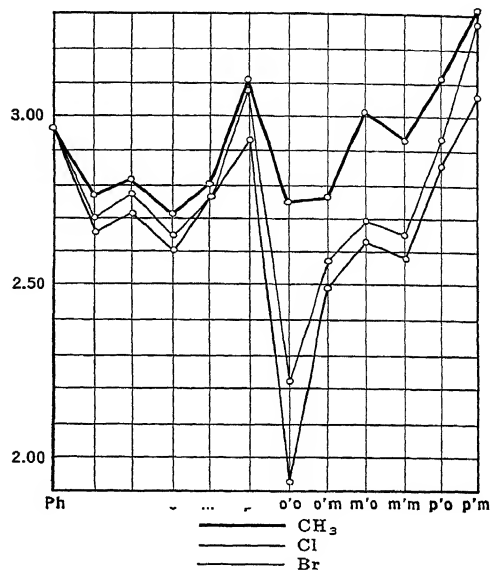
Fig. 2. Extinction Values of the Indicated Compounds in Hydrochloric Acid.

4. In the disubstituted compounds the increases or decreases of magnitude of the absorption bands bear little mathematical relation to the effects produced by the constituent groups themselves.

5. In the p'-o disubstituted compounds the p' substituent seems to exert a stronger influence on the frequency of absorption maximum in alcohol, while the o substituent has more effect on the extinction of the absorption band. In hydrochloric acid and sodium hydroxide there seems to be little relation of effect to position.

6. In all solvents, the extinction of the absorption band for a given bromo compound is either equal to or slightly greater

than that of the corresponding chloro compound, regardless of position of substitution.

7. The principal absorption bands of these compounds in sodium hydroxide appear to consist of two overlapping bands,
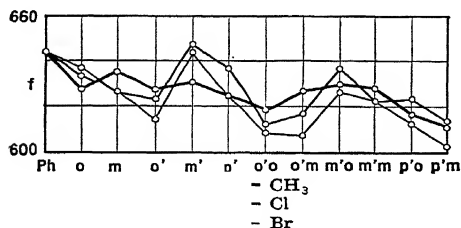
tions of substitution, whereas the extinction values of the separate components seem to show little relationships.

The unusual effect of substitutions placed adjacent to the chromophore (azo) group in either the meta or ortho prime
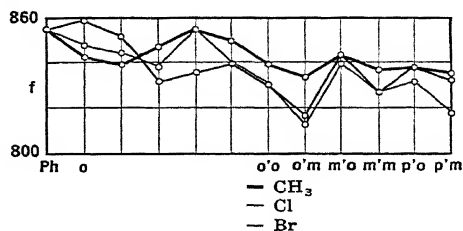
FIG. 3. (Left) Frequencies of the Absorption Maxima of the Indicated Compounds in Hydrochloric Acid. (Right) Frequencies of the Absorption Maxima of the Indicated Compounds in Alcohol.
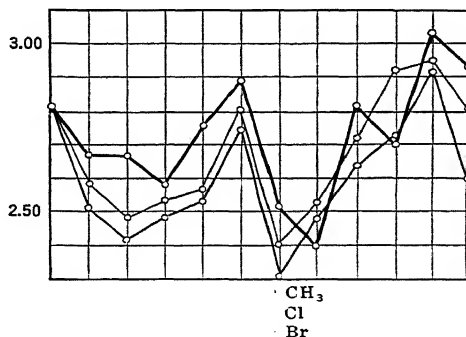
FIG. 4. Sum of the Extinction Values of the Components (a b) of the Absorption Bands of the Indicated Compounds in Aqueous Sodium Hydroxide.

which are believed due to two forms of vibration of the molecule, present in an equilibrium. Analysis of these compound bands into their components gives information concerning the effect of position isomerism on this equilibrium. The chloro derivatives appear to exist in four equilibrium levels, whereas the bromo derivatives appear to exist in six levels.

8. The sums of the extinction of the components of the principal absorption band in sodium hydroxide solution appear to bear general relationships to the posi-

position leads to the general subject of chelating or ring formation properties of active groups adjacent to the azo or other chromophoric groups and the formation by metal salts of complexes or coordinated dyestuffs. This subject was discussed in a previous paper and has been further investigated. The special case investigated involved the coordination of metal salts with ortho hydroxy azo dyes. In our previous discussion we pointed out that this combination was bimolecular in character, two molecules of dye combining with one

of the metal salt. The nature of this combination was postulated as a chelated ring of uncertain size.

To define more accurately the size of this ring a spectrophotometric study was made of the coordinated metal complexes of simple azo dyes and a series of simple organic compounds which possess certain structural parts in common with part of the azo dye complex.

A study of the azo dye structure indicates the following possible arrangements:
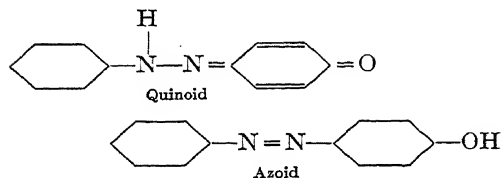
Quinoid

Azoid

It might be explained that the terms quinoid and azoid refer in this equation to an equilibrium or resonance between two dynamic isomers. It is not intended that the quinoid formula should indicate a destruction of the benzene ring, and it might be more to the point to use the electronic formulas of Wizinger to indicate the shift of electron arrangement rather than complete valence bonds.
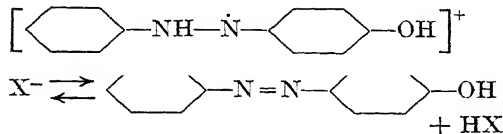
The metal complex produced from phenyl azo-*p*-cresol
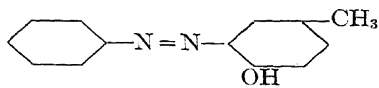
may be indicated as azoid or quinoid structures.

(1) Azoid

(2) Quinoid
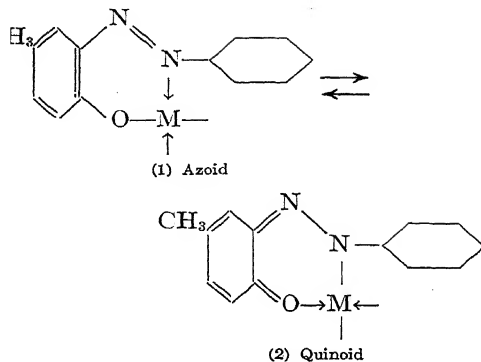
These structures being considered as merely representative of two resonating forms, the problem resolves itself into the determination of the distribution of these forms in the complexes.

A study of the absorption spectra of a series of related compounds gave the following data shown in Table III, where types 3 and 4 represent azoid and quinoid forms.

(3)

(4)
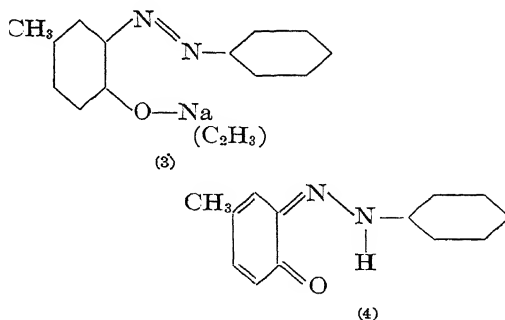
From the fact that the method of synthesis of the ethyl derivative requires a type 3 structure, it is possible to assign the absorption band at 620-650 f to that form, and the observation of the bond at 750-760 f in this absorption spectra allows us to assign the latter band as characteristic of the type 4 structure.

The absorption spectrum of the copper complex shows both of these bands and allows the deduction that an equilibrium exists between types 3 and 4.

TABLE III

ABSORPTION SPECTRA OF PHENYLAZO-*p*-CRESOL

Deriva-tives	Bands (f)			Type
Na	620		910	3
H		750	920	4
C_2H_5	650		990	3
Cu	630	760	930	$1 \leftrightharpoons 2$

This same method of structural analysis being applied to the simpler case of salicylaldehyde, the data in Table IV were obtained.

From these data and the known fixed position of the methyl derivative it has been possible to assign type 1 structure to the OH and OCH_3 whereas the Na salt is given a quinoid structure (2). Like the more complex azo dyes the metal coordinated structures show both band systems and are characterized as in equilibria between the two forms (3).

Some doubt still remains, however, as to the actual size of the chelate ring formed by the metal, and a further study has been made of the absorption spectra of the free hydroxy and copper complex of the Schiff's base formed from benzaldehyde and *o*-aminophenol (*a*) and the Schiff's base formed from salicylaldehyde and aniline (*b*). According to our ideas and knowledge of partial and coordinated valence in this series of compounds the first one (*a*) is capable of forming only a five-membered chelate ring while the latter one (*b*) can form only a six-membered chelate ring.

TABLE IV

ABSORPTION SPECTRA OF SALICYLALDEHYDE

Derivative	Bands			Type
	I	II	III	
H		925	1185	1
Na	780		1190	2
Cu	760	930	1190	3
Ni	790	920	1190	3
Co	790	910	1190	3
CH_3		930	1190	1
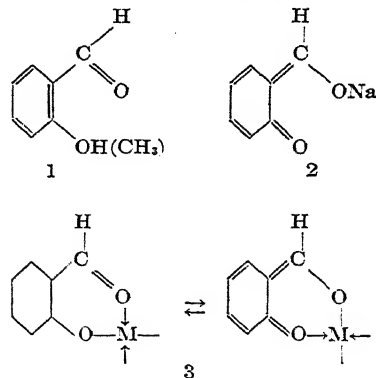
From these data it appears that little energy or structural difference is produced in the molecule by this five- to six-membered coordinated ring change and hence the prediction of the size of the chelate ring in the azo dyes is still somewhat uncertain.

REFERENCES

1. For further references see *J. Am. Chem. Soc.*, 56, 1037 (1934).
2. BRODE, *ibid.*, 51, 1204 (1929); *Bur. Standards J. Research*, 2, 501 (1929).
3. BRODE, Ber., 61, 1724 (1928).

PHOTOCHEMISTRY OF THE VISUAL SPECTRUM

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Some experiments carried out recently in the Chemistry Department of the University of Glasgow have been concerned with new and more specialized ways of dealing with the problems which the phenomena of photodichroism and color adaptation present to the investigator. It has long been noticed that both phenomena occur most frequently in the visual range of the spectrum, and it is to be expected that an extension of our knowledge of this range may be of use for the study of the chemical action of this type of radiant energy, which is most important for photography, for vision, and for utilizing solar energy.

Photodichroism, which was discovered about twenty years ago,[1] occurs when plane-polarized light produces dichroism by striking isotropic systems which contain colored light-sensitive particles. Systems which are particularly suitable for the production of photodichroism are solid gelatin or collodion films.

The optic axis of the photodichroic system is parallel to the orientation of the electric vector of the plane-polarized light by which the effect was produced. Therefore, photodichroism means the stabilization of the plane of polarization.

The phenomenon occurs very frequently. The majority of dyestuffs imbedded in gelatin or collodion were tested with posi-tive results,[2-8] and gelatin emulsions containing silver salts with or without photographic development are suitable for producing the effects.[9-17] But gelatin or collodion is not an indispensable component of the system, for silver halides[16-19] and certain thixotropic dyestuffs[20] without binding medium can become photodichroic as well.

It is almost generally accepted at present that the production of photodichroism by exposing the systems to plane-polarized light is due to the presence of minute dichroic and light-sensitive particles which are distributed at random in the system before the exposure. The plane-polarized light affects selectively those particles, the axes of which are situated in or perpendicular to the plane of polarization. By photochemical action the color of the particles with axes which are preferentially parallel is changed, which makes the whole system dichroic.

Photodichroism is therefore an adaptation of the exposed system to the vibration of light. It is associated frequently with color adaptation, which means an adaptation of the system to the maximum wavelength of the exposing colored light. Taking into account an explanation similar to that of photodichroism, the dichroic particles must have various maxima of absorption distributed over the whole visible

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spectrum. This can occur only if the particles are built up from different components with a certain latitude of distribution and size.

This property is due essentially to colloidal particles or micelles, but according to Wiener's theory of mixed bodies the particles responsible for photodichroism and color adaptation must have distances from each other and sizes which are smaller than light waves. The micelles belong
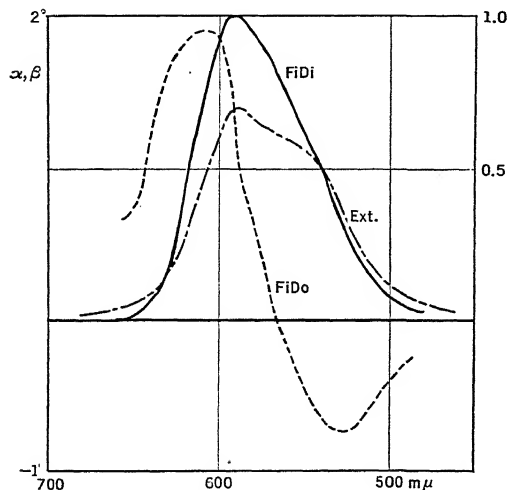
FIG. 1. Crystal-violet Collodion.

therefore to the amicroscopic range of sizes, and ultramicroscopic resolution cannot be expected.

Now the question arises of the nature of the micelles, which can be dealt with only by polarimetric methods. The problem could be solved easily if the photodichroism of collodion films stained by organic dyestuffs is considered. Here the dichroic particles are minute fibers of nitrocellulose having adsorbed dyestuff molecules.

The presence of such colored nitrocellulose micelles before the exposure was proved by experiments during recent years

in studying a specific quality of colored collodion films called *film dichroism* (FiDi). The dichroic behavior of such a film when polarized light passes through it
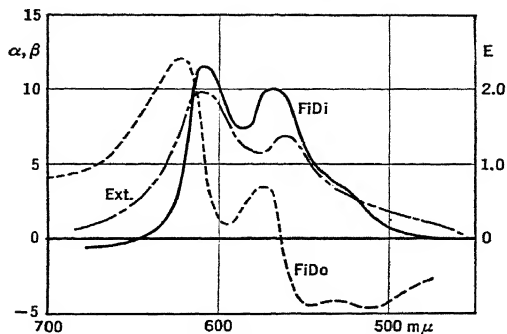
FIG. 2. Pinacyanol Collodion.

obliquely is due to film dichroism. A very convenient device has been developed to study film dichroism by means of a purely differential method which is quite similar to my polarimetric method for determination of photodichroism, which has been adopted by most investigators.

This method, which enables one to measure the whole dispersion curve of film-dichroic systems very quickly, will be described in detail in another paper.

Film dichroism of collodion films is of course due to the fact that the axes of the minute nitrocellulose fibers are situated at random only in the plane of the surface of the glass plate which had been coated with solution of collodion. The sign of film dichroism was taken positive if a polarized light beam passing obliquely through the film was absorbed mostly when the light vibrates perpendicular to the plane of incidence.

Figs. 1 and 2 show for crystal violet and pinacyanol collodion the extinction (Ext.), film dichroism (FiDi) and film double refraction (FiDo) plotted over a wavelength scale. FiDi and FiDo are linked by Zochers

rule.[21] The validity of this rule according to which the sign of FiDo is inverted near the wavelength of maximum FiDi is quite evident for crystal violet. For pinacyanol
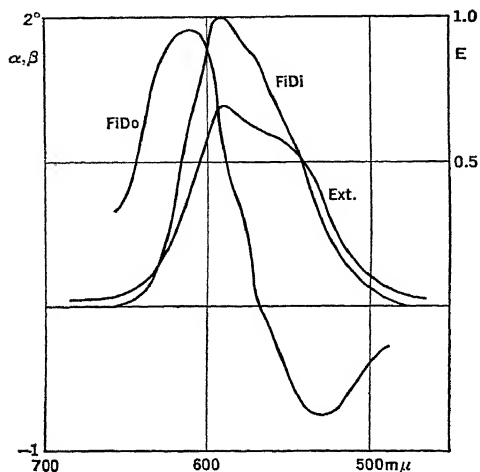
FIG. 3

the effects of two maxima of FiDi are superimposing each other in the curve of FiDo.

Colored gelatin films exhibit also FiDi, which is due to a tension of the film in its plane, but as can be seen from Figs. 3 and 4 the extinction curves and FiDi of pinacyanol and pinachrome are not closely related to each other as with collodion films.*

If a colored film is exposed to *natural* light its absorption is altered owing to a photochemical reaction and at the same time its film dichroism is changed (Fig. 5). The *difference* of FiDi before and after the exposure is called photo film dichroism (PhFiDi). Fig. 6 shows PhFiDi of a crys-

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* These differences indicate that the dyestuff molecules exist in collodion over gelatin films in different states. The detailed study points to single molecules in collodion films and to larger complexes in gelatin films.

tal-violet collodion film after an exposure to *natural* light and the photodichroism after exposure of the same film to *polarized* light. Both graphs exhibit a negative effect in the green and positive effects in the red and blue part of the spectrum. This makes it probable that in both cases the same particles are responsible for the optical changes. The anisotropic and dichroic properties are forced upon the dyestuff particles by the binding medium with its fibers parallel to the surface of the glass plate, and the optic axes
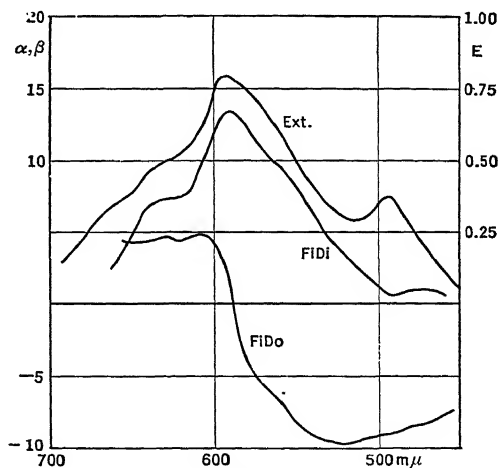
FIG. 4

are situated in the plane of the film. We shall call such particles *particles of the first kind.*

Still another kind of dichroic particles occurs in these systems, particularly in gelatin emulsions of silver halides and to a less extent in dyestuff films, which may be distinguished by the term *particles of the second kind.* Their existence was revealed during the very first experiments on photodichroism[9] on exposing to polarized light isotropic gels of photochloride gelatin

in which no tension occurred. Effects of photodichroism were observed which were quite similar to those exhibited by solid gelatin films. Even natural light was observed to produce them when the exposed
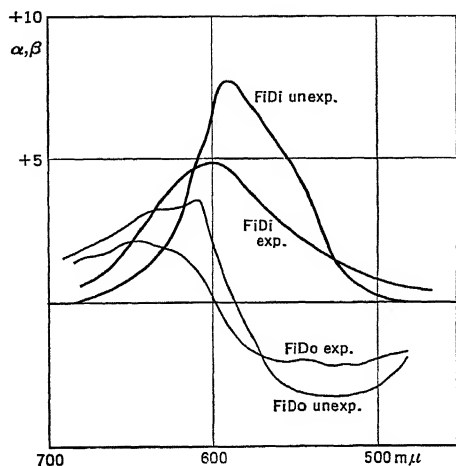
FIG. 5

gel was viewed perpendicularly to the exciting natural beam.[9, 16] This phenomenon is analogous to the production of polarized Tyndall light or polarized fluorescence by natural light under the same conditions of experiment. The axes of the dichroic particles which were altered by the exposure are situated in planes which are perpendicular to the exciting natural beam.

The investigation of these particles in gels was very difficult and it was abandoned after their existence had been established. But a slight modification of the recent experiments on film dichroism offered a very speedy and convenient method to study them by using natural light for excitation, and it is now possible to separate neatly the properties of the particles of the first and of the second

kind which always were superimposed upon each other in previous experiments with polarized light.

The general principle of the method can be understood from Fig. 7. The bodies represented perspectively show a prismatic piece cut from the solid film and greatly enlarged. The dotted areas mark the planes in which the axes of the dichroic particles are situated.

In the upper series occur particles of the first kind only with the axes *parallel to the plane of the film*, e.g., in colored nitrocellulose fibers. If such a film is exposed under 45° to natural light as marked by the arrow indicated by dashes, which can be made easily by immersing the film in a trough containing benzene, the micelles change their color photochemically. On
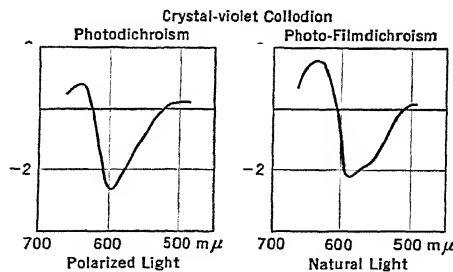
FIG. 6

observing them parallel to the exciting beam by placing the exposed film between the polarizer and analyzer of the polarimeter in the same position A as marked by the solid arrow, *photo film dichroism* is established. This was indicated by an ellipse under the first graph. Now the film is turned through 180° *in its plane* into the position B, which makes the beam for observation intersect the direction of excitation by 90°. No change of the dotted plane happens by this operation and the same amount of PhFiDi can be read. Finally, on observing normally the exposed film in

the position C no film dichroism at all can be detected because the light used for the exposure was natural. The circle under graph C indicates this isotropic behavior.

In the lower series of Fig. 7 the dichroic particles of the second kind produced by the exposure to natural light *have their axes in planes perpendicular* to the exciting beam, and on observing the film in position A in the same direction no dichroism can occur. By turning the film again into position B the dotted plane is met by the observing beam on edge and strong dichroism can be read. Indeed, we have the same conditions before us as in the gel which was observed perpendicular to the exciting beam. In the last position C the plane containing the axes is observed under $45°$ and a smaller dichroism is expected.

It is evident that in an actual experiment when both kinds of dichroic particles are present their optical properties can be determined separately because they influence differently the dichroism read by the polarimeter in the positions A, B, or C. E.g., in position A only the particles are effective which are due to the anisotropy of the binding medium; in position C, only those particles the axes of which coincide with the vibration of the exciting beam; and in position B both kinds of particles produce dichroism, but because the effect of the particles of the first kind is the same in the positions A and B the *difference of the values $B-A$ corresponds exclusively to* the dichroism produced by the particles of the second kind. The readings in the positions B and A and their difference will
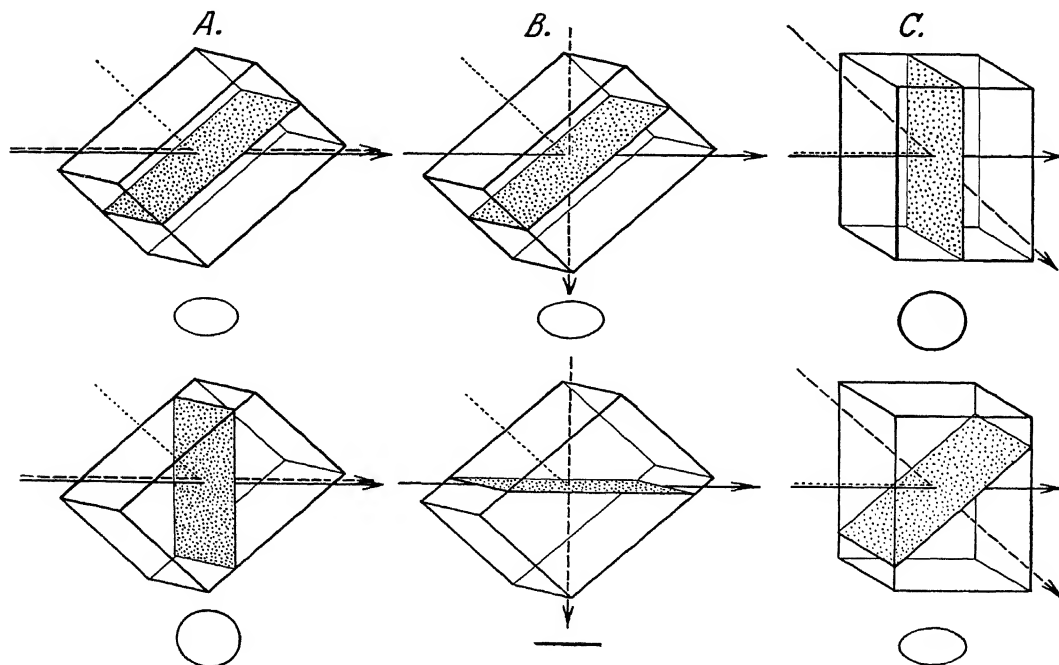
FIG. 7

therefore do to analyze the particles with respect to their optical properties.

Experiments in this direction are now in progress, and the whole material on photo-dichroism accumulated during the last 20 years ought to be revised from this new standpoint. Of course, only a very small portion of this research could have been done previously. Here only a few experiments which dealt with gelatin emulsions containing silver chloride or silver bromide with a slight excess of silver ions will be discussed.

Fig. 8 shows the dichroism read in the position A, B, and $B-A$ with *silver chloride* gelatin. The graphs are plotted in degrees read at the analyzer of the polarimeter over a wavelength scale. Various spectral ranges isolated by filters from a carbon arc

were tested: ultraviolet with a center of gravity at about 390, violet at about 410, blue at about 450, and the green at about 530 mμ. All red light was eliminated by a copper sulfate filter except in one case when two dark cobalt glasses without copper sulfate were used (blue + red), which allows a trace of dark red light being effective, superimposing the blue light being used for the blue exposure. The coloration of the five exposed fields was brought roughly to the same darkness.

Readings in position A show that the film dichroism of the silver produced photochemically is *positive* over the whole spectrum range from 680 to 480 mμ, and the values are almost alike for the various colors of the exposing lights. But B and $B-A$ reveal remarkable differences due
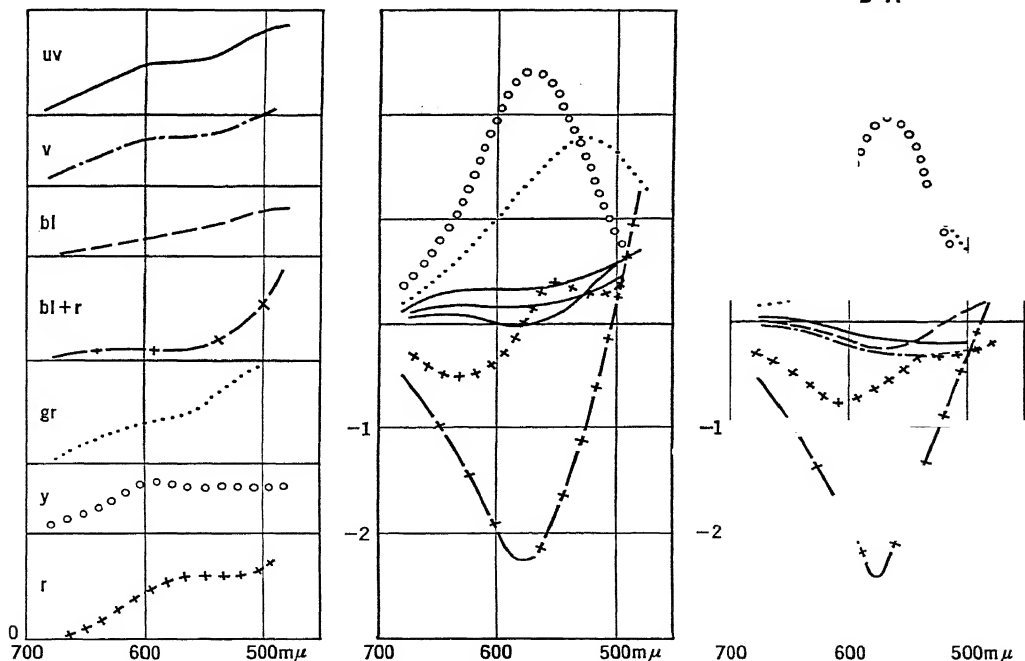
FIG. 8

to color adaptation. This can be seen particularly from the dotted graph for green with its minimum in the green part of the spectrum which means maximum *transparency* for the exposing color. The graph for pure blue light becomes negative at the blue end of the spectrum. Compared with this curve the (blue + red) curve demonstrates remarkably the dan-

the production of silver by photolysis. The filter for yellow light was made up from one trough filled with potassium dichromate and another one with copper sulfate excluding red light, and the filter for red light was transparent from 600 mμ upwards.

As can be seen from Fig. 9, again the film dichroism is positive in position A
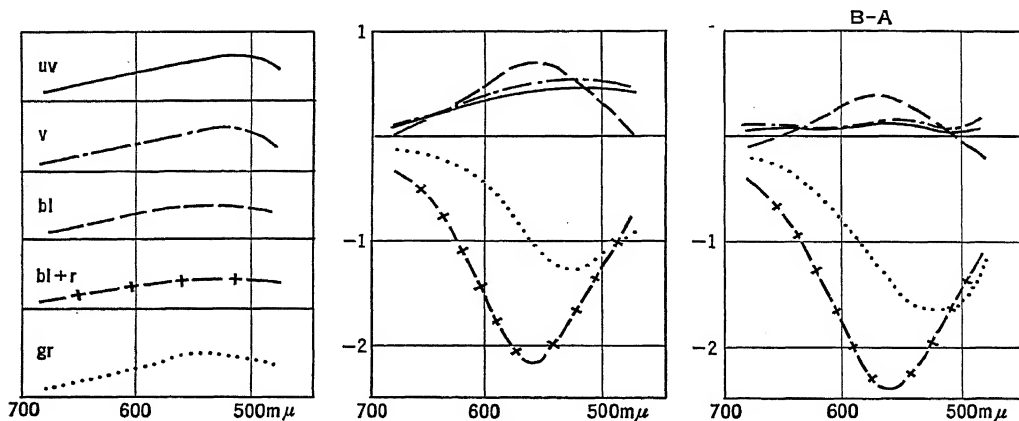
FIG. 9

gerous influence of red light during these experiments. The unexposed emulsion of silver chloride was not sensitive to longer wavelengths than green, but when blue light produces simultaneously some silver a strong sensitizing for red light is brought forward and the dichroic effects arise which are well known from previous experiments on photodichroism.

These experiments have established indubitably that the specific action of colored light in silver chloride emulsions is due exclusively to the presence of particles of the second kind.*

Now *silver bromide* was studied, Fajans'[22] researches on the sensitizing action of adsorbed silver ions on the faces of silver bromide crystals paved the way for proceeding even to yellow and red light for

for all colors but there happen distinct differences with respect to the magnitude

*The nature of these dichroic systems could be established more determinately by some experiments carried out during recent months. (F. Weigert, *Photogr. J.*, Feb., 1939.) The important parts of the light-sensitive gelatin films are silver halide crystals with small quantities of silver adsorbed to their surfaces. The primary effect of light is the expulsion of an electron from a silver atom to be caught by a near silver ion belonging to the silver halide crystal. The dichroic systems of the second kind can therefore not be considered as " particles " but rather as the spots or the areas of contact where the silver is adsorbed to the crystal. The lines of linking between the silver atom and the silver ion correspond to the axes of the dichroic systems. They are oriented in all directions in space and not only in the plane of the film as happens with the axes of the particles of the first kind, e.g., the colored nitrocellulose fibers.

of the effect. But the graphs in *B–A* reveal quite new optical features which may be called negative color adaptation. It follows unmistakably from the graphs for green and yellow exposure that their *maxima* are situated in the respective ranges of the spectrum. The same tendency can be expected from the graphs for blue and even for violet and ultraviolet light.

This means that the particles *produced by a certain colored light absorb just this light*. This is a photochemical phenomenon which occurs only in a very few cases.

Blue + red affects film dichroism again quite anomalously, and red, a color which gave clear effects in all previous experi-

ments on photodichroism behaves in a very complicate manner. This can be seen from Fig. 10, which demonstrates the effect of red light of various intensities. The exposure times were adjusted to produce almost the same coloration on the silver bromide gelatin film, and from the table in the *A* section of Fig. 10 can be read that the total energy striking the film was always of the same order. But from the graphs in the positions *A, B,* and *B–A,* enormous differences of the optical properties of the particles produced by the red exposure follow. They may be of interest for photographic science because they are examples of extreme failures of the reciprocity law. They are caused by the oc-

i	t	it
1	60'	60
2.25	20'	45
5.75	8.5'	46
16	3.75'	60

Red
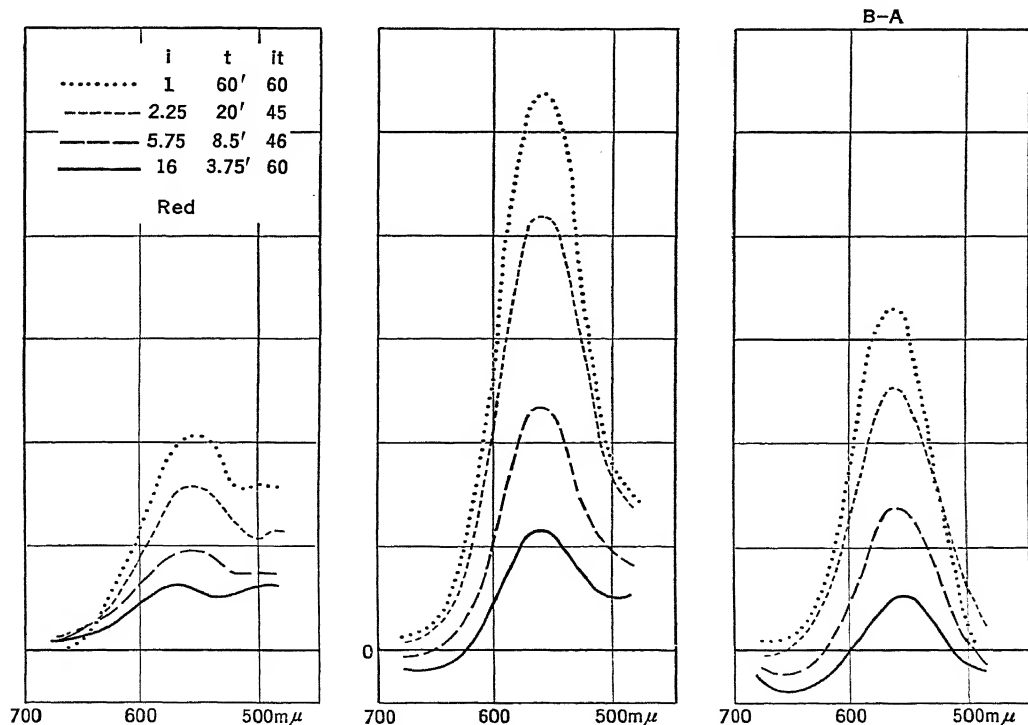
Fig. 10

currence of a new time phenomenon in photographic emulsions which was discovered some months ago.[23] It was revealed that the activity of a silver sensitizer for red light is not constant but that it is reduced in the course of some minutes. In the experiments under study here, with pure red lights effective during different periods but with the same total energy, it is to be expected that the dichroic effects typical for red light must be less pronounced the longer the exposure time is. When blue light acts simultaneously as in the experiments with (blue + red) exposure the sentitizer is extremely active.

The discussion of the experiments reported here and of their meaning for the explanation of photodichroism, film dichroism, and the photochemical phenomena occurring in photographic emulsions and in stained films will be dealt with in another paper.

Summary. " Photodichroism " occurs when colored and light-sensitive films are exposed to plane-polarized light, with preference in the visible range of the spectrum. This phenomenon is due to the existence of minute dichroic systems which are affected selectively when their optic axes correspond to the vibrations of the polarized light with respect to the orientation. The same dichroic systems make the unexposed dichroic when light passes through it obliquely. This optical property is called " film dichroism."

Quantitative experiments on film dichroism of colored films and on its changes after exposure of the film to natural light revealed that there exist two kinds of dichroic systems with different properties which can be separated by a special experimental technique. In photographic emulsions containing silver salts the specific action of colored light is due only to the systems of the second kind the dichroism of which is not originated by the anisotropy of the binding medium in the film.

ACKNOWLEDGMENT

REFERENCES

1. F. Weigert, *Verhandl. deut. physik. Ges.*, 21, 479 (1919).
2. F. Weigert, *ibid.*, 21, 623 (1919).
3. H. Zocher and F. C. Jacobi, *Kolloid-Beihefte*, 24, 365 (1927).
4. F. Weigert, and M. Nakashima, *Z. physik. Chem.* (B), 4, 258 (1929); 7, 25 (1930).
5. T. Kondo, *Z. wiss. Phot.*, 31, 153, 185 (1932).
6. F. Matulis, Thesis, Kaunas, 1934, *Kolloid-Beihefte*, 38, 384 (1933).
7. W. Kemula, *Z. physik. Chem.* (B), 23, 305 (1933).
8. G. Ungar, *ibid.*, 38, 427 (1938).
9. F. Weigert, *Ann. Physik*, (4), 63, 681 (1920).
10. F. Weigert and E. Elvegard, *Z. physik. Chem.* (B), 4, 239 (1929).
11. F. Weigert and F. Shidei, *ibid.*, 9, 329 (1930).
12. F. Weigert and Stiebel, *ibid.*, 13, 285 (1931).
13. F. Weigert and E. Eberius, *Kolloid-Z.*, 58, 276; 60, 13 (1932); 62, 306 (1933).
14. H. Zocher and K. Coper, *Z. physik. Chem.*, 132, 311 (1928).
15. E. Mathieu, *Rev. optique*, 9, 253 (1930).
16. A. E. Cameran and A. M. Taylor, *J. Optical Soc. Am.*, 24, 316 (1934).
17. H. Zocher and K. Coper, *Sitzber Preuss Akad. Wiss.*, 426 (1925).
18. K. Umrath, Dissertation, Göttingen, 1930.
19. S. Tcherdyncev, *IX. Congr. intern. phot. sci. appl.*, 1935.
20. W. Kuhn and G. Erdoes, *Kolloid-Z.*, 70, 241 (1935).
21. H. Zocher, *Naturwissenschaften*, 13, 1015 (1925).
22. K. Fajans, *Z. Elektrochem.*, 28, 499 (1922).
23. F. Weigert, *Trans. Faraday Soc.*, July, 1938.

CONVERSION OF LIGHT INTO CHEMICAL ENERGY

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The purpose of this paper is to discuss an aspect of photochemistry which has been somewhat neglected recently. Helmholtz[1] in 1847, E. Warburg[2] in 1907, and Weigert[3] in 1911 have all emphasized the distinction between "work-producing" and "work-accumulating" photochemical reactions. In the first type light accelerates a process which is thermodynamically possible in the dark. In the second type, light is partially converted into potential chemical energy and the free energy of the system is increased.

One year after the publication of Weigert's monograph Einstein[4] enunciated the law of photochemical equivalence, and attention turned to the investigation of its consequences. More recently detailed investigations of the kinetic mechanism of photochemical reactions have supplanted simple determinations of the quantum yields. The intention is usually to find out what happens to all *material particles* taking part in the process; less interest is paid to the fate of the *light energy* used in its initiation.

The conversion of light energy into chemical energy remains an important problem, however, especially in consideration of its practical importance for energy supplies on earth.

In discussing this subject today not many new examples can be added to those discussed by Weigert 27 years ago. On the other hand, our increased knowledge of the interaction of matter and light shows us new lines of approach to this problem.

From the point of view of atomic physics, the essential differentiation is not that between work-liberating and work-accumulating reactions, but between reactions involving a decrease or increase of electronic energy. The dissociation of NH_3 into $\frac{1}{2} N_2$ and $\frac{3}{2} H_2$ increases the electronic energy by 14 Kcal per mole, at all temperatures and concentrations. The characteristics of the photochemical process are the same when NH_3 decomposition brings the system nearer to the thermodynamic equilibrium as when it removes it from it.

The exact measure of the change in electronic energy is Q_0, the heat effect of the reaction at absolute zero. For reactions with a heat effect larger than 2-3 Kcal per mole, the sign of Q_0 is identical with that of the heat effect at room temperature.

Most of the best-known photochemical processes are *exothermal* $(Q > 0)$. All *chain reactions* belong to this class. In the hydrogen-chlorine reaction, the absorption of one mole of photons with an energy of 70 Kcal causes the formation of several thousands moles of HCl, liberating up to 200,000 Kcal of heat. The chlorination of CO, the decomposition of ozone, and the

oxidation of HI are other examples of the same kind.

A quantum yield $\gamma \gg 1$ is a certain indication of an exothermal reaction. Most of the photochemical reactions with $\gamma \leq 1$ are, however, also exothermal ones, light playing only the part of activation energy. Chlorination and bromination of organic compounds, oxidation of aldehydes, and bleaching of dyestuffs are examples of this kind.

In a number of photochemical reactions, a certain proportion of light energy is converted into chemical energy. In the photochemistry of organic compounds, this proportion is perforce a small one, since organic substances have already a high content in chemical energy and not much can be added without making the system totally unstable (e.g., by producing free radicals). The "activation" of organic compounds (e.g., of ergosterol) by ultraviolet light, the isomerization of fumaric acid, and the polymerization of anthracene are examples of reactions in which a small proportion of light energy (of the order of 5-10 per cent) is transformed into electronic energy of the products.

For wider possibilities of conversion we have to turn to inorganic compounds. Inorganic substances which absorb light in the visible region are usually photochemically stable. The absorption by colored cations, Ni^{2+}, Co^{2+}, and Mn^{2+}, as well as numerous complex ions, is due to transitions between two states belonging to the same fundamental electronic configuration and does not "activate" the ion chemically. Conditions are different for less stable cations, e.g., Fe^{3+}, Ni^{3+}— complexes, etc. These ions can be reduced by light; they also can act as photosensitizers. Colored anions (chromate, permanganate, etc.) are also photochemically active. Many single observations exist in this field (see, e.g.,

Dhar's[5] book), but not much is known about the mechanism of these reactions, and practically nothing about their energetical effects. In this connection the photochemical reduction of water by Fe^{2+} ions (J. Weiss[6]) and its photochemical oxidation by Ce^{4+} ions (J. Weiss and Porret[7]) are of interest. Both reactions are certainly endothermal, but the amount of energy stored is unknown. These reactions require ultraviolet light.

The best-known photoreaction of ionic compounds is the dissociation of silver bromide. The latent image can be produced with $\lambda \leq 5000$ A (55 Kcal per mole) without sensitization, and with $\lambda \leq 1.3$ (28 Kcal per mole) with sensitization. The dissociation energy of AgBr into metallic silver and gaseous bromine is 27 Kcal per mole. If the photochemical process is AgBr $\rightarrow \frac{1}{2}$ Br_2 + Ag, the "energetical yield" is up to 50 per cent in the non-sensitized plate and > 100 per cent in the sensitized plate (if only one photon takes part in the reduction of one AgBr molecule). However, the process is complicated by the acceptor action of the gelatin, by a possible participation of the sensitizing dye, and by the part which Ag_2S may play in the formation of the latent image. Experiments of Blair and Leighton[7a] have shown that only 15 Kcal are required for one *thermal* production of the latent image (and not 28 Kcal). Even this figure indicates, however, the possibility of an efficient conversion of visible light into chemical energy by ionic compounds.

Energetical yields of the order of 50 per cent are not uncommon in reactions of inorganic compounds in extreme ultraviolet light. Dissociation of water into H_2 and O_2 by light < 2000 A, and the — better-investigated — ozonization of oxygen by light $\lambda 2070$ A (E. Warburg[8]), are examples of this kind. The photons used in these re-

actions correspond to 140-150 Kcal per mole; the amount of electronic energy accumulated in these reactions:

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 \text{ and } 3 O_2 \rightarrow 2 O_3$$
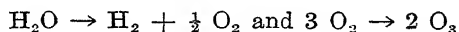
is about 70 Kcal.

Nature provides us with by far the most efficient process of conversion of visible light into chemical energy — the assimilation of carbon by green plants. It is often assumed that assimilation is primarily the reversal of the combustion of formaldehyde:

$$CO_2 + H_2O \rightarrow H_2CO + O_2 - 135 \text{ Kcal (1)}$$
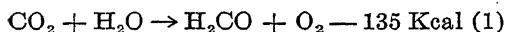
According to O. Warburg,[9] under most favorable conditions 1 molecule of CO_2 is reduced by 4 quanta of visible light; these results have been doubted by certain investigators[10] but have recently been confirmed by Franck and Rieke.[11]

The light energy consumption is, at 6600 A (maximum of the chlorophyll absorption band), $4 \times 43 = 172$ Kcal per mole CO_2. This means, according to (1), an energy yield of about 80 per cent. However formaldehyde has never been actually observed as an intermediate product, and it is safer to make the calculation on the basis of the assimilation products found in the plant — e.g., sugars. The assimilation reaction is then

$$Co_2 + H_2O \rightarrow \tfrac{1}{6} C_6H_{12}O_6 - 112 \text{ Kcal (2)}$$
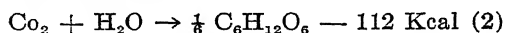
Even in this reaction the utilization of light energy is about 70 per cent. This high yield is especially astonishing in a 4-step reaction, in which the low-energy system $CO_2 + H_2O$ is lifted to the high energy level of the organic world by the successive absorption of 4 quanta. The reaction must involve three intermediate states, all stable enough to await the arrival of the next photon without an appreciable back reaction taking place in the meantime. So far chemists have been unable to iden- tify a single one of these intermediate products. Thus, the mechanism of the assimilation process remains an intriguing puzzle.

High efficiency of photosynthesis is observed only at low intensities of illumination (about 1/50 of the intensity of sunlight). At the higher intensities a "saturation" occurs, the reduction rate becoming independent of the light intensity. The energy conversion yield decreases correspondingly. In grass and leaves on a sunny day, this yield is on the average of the order of 5 per cent. (Compare Pütter; Spoehr; Boysen-Yensen; and Bose.[12])

Light saturation seems to be a natural device to protect the plants — which literally swim in food — from overfeeding. There is nothing impossible in the idea that this limit can be lifted, by appropriate selection, or by artificial enzymatic stimulation. (The last possibility is indicated, e.g., by some experiments by Bose).

The lack of success of attempts to reproduce photosynthesis in vitro must be due not only to the failure of reproducing the complete *chemical* system present in the plant, but also to our incapacity of providing *physical* conditions necessary for the effective accumulation of quanta. The photosynthetic apparatus in plants is certainly a heterogeneous one, and adsorption effects play an important part. It has been suggested (by Arnold, Emerson, Gaffron, Wohl and Weiss[13]) that chlorophyll is present in the plants in the form of "photosynthetic units" — particles adsorbing CO_2 and H_2O on their surface — and that light absorbed anywhere in the interior of these units is available, by a process of resonance transfer, for a photochemical action on the surface. This mechanism (which possibility is, however, doubted by Franck and Teller[14]) could,

contribute efficiently to the concentration of 4 quanta on 1 molecule of CO_2.

In the reduction of CO_2, nature shows that a reaction which, in a homogeneous system of pure components, requires extreme ultraviolet light, can be made to proceed in visible light by the use of the following implements:

(a) *Sensitization* by a dyestuff absorbing in the visible.

(b) *Catalysis* (homogeneous or heterogeneous), i.e., the provision of substances helpful in the formation and stabilization of the intermediate products.

According to the theory of the photosynthetic unit, a third point should be added:

(c) *Quantum accumulation* by resonance transfer.

Chlorophyll solutions — molecular and colloidal — are insufficient to reproduce protosynthesis. A first step towards a more faithful reproduction of the natural conditions has been made recently by the extraction of an intact chlorophyll-protein complex (which is destroyed by the usual extraction with organic solvents).

What should be stressed in this connection is that the principles used by nature in photosynthesis *must be capable of a more general application*. The following reactions are some examples of endothermal processes which can be achieved, in molecular disperse homogeneous systems, only by means of ultraviolet light.

$$CO_2 \rightarrow CO + \tfrac{1}{2} O_2 - 58 \text{ Kcal} \qquad (3)$$

$$H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 - 58 \text{ Kcal} \qquad (4)$$

$$N_2 + O_2 \rightarrow 2 NO - 43 \text{ Kcal} \qquad (5)$$

$$C_2H_6 \rightarrow C_2H_4 + H_2 - 41 \text{ Kcal} \qquad (6)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 - 35 \text{ Kcal} \qquad (7)$$
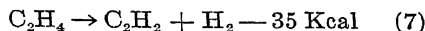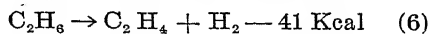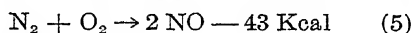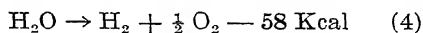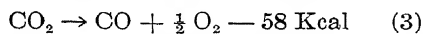
Whereas the photosynthetic reaction (1) involves the breaking of 4 bonds and requires correspondingly 4 photons, the above reactions — with the possible exception of (5) — involve the disruption of only 2 bonds and could therefore be achieved in two steps, if an appropriate sensitizing system could be found. It is reasonable to assume that the solution of this problem must be simpler than the reproduction of photosynthesis in vitro. Each of these reactions, if carried out with a satisfactory quantum yield in visible light, would represent a successful solution of the problem of utilization of light energy.

We have, of course, no direct indications how to attack this problem, whereas in photosynthesis the plants show us the solution. The principles, however, must be the same: sensitization, catalysis, and accumulation of quanta. The first principle means the use of dyes; the two others the use of a heterogeneous system instead of a homogeneous one. Systematic experiments on the photochemistry of substances adsorbed on colloidal dyestuffs represent a possible line of approach.

An indication to the possibility of new effects produced by the cooperation of a great number of chromophores in a colloidal particle is found in recent work by Scheibe.[15] Experiments on the accumulation of quanta in mercury vapor by resonance (Beutler and Rabinowitch[16]) are also of some interest in this connection.

We have considered so far the *irreversible* conversion of light energy into chemical energy. A number of photochemical reactions in which light energy is converted into chemical energy are immediately *reversible*. As soon as the illumination ceases, the system returns to its original state of low energy. Sometimes the back reaction is also accelerated by light. Examples are the " light equilibria " or, more exactly, " stationary states " investigated by Coehn and co-

workers.[17] The systems $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$, $HCl \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}Cl_2$, etc., when illuminated by "white" light, assume a stationary dissociation state: light absorbed by H_2O (or HCl) causes the dissociation; light absorbed by O_2 (or Cl_2) accelerates the recombination. Analogous processes occur in the visible spectrum. Holst[18] found, for example, that the oxidation-reduction equilibrium of the dyestuff system

$$C_6H_5NH \cdot NH \ HSO_3 + \text{Methylene blue}$$
$$\rightleftharpoons C_6H_5N = NHSO_3 + \text{Leuko-}$$
$$\text{methylene blue} \qquad (8)$$
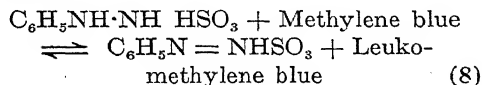
is shifted "to the right" by yellow light (which is absorbed by methylene blue) and "to the left" by blue light (absorbed by phenyldiazosulfite).

We have investigated some reversible reactions in which the back reaction is a purely thermal one.[19] With very quick back reactions, intense illumination is required for a measurable shift of the equilibrium, and even then the shift is detectable only by very sensitive instruments. A chemical system can be illuminated by the light of a carbon arc and the change in the stationary concentration of the light-absorbing substance during the illumination be measured by means of a photoelectric photometer based on the compensation principle and indicating extinction changes of the order of 0.005 per cent and less. Fig. 1 shows a typical set of measurements. The points represent the extinction of the system measured alternately with the vessel in the dark and exposed to strong light. The reversible bleaching effect in this particular case is of the order of 0.05 per cent, i.e., one light-absorbing molecule in 2000 is in the "bleached" state during the illumination. Since under the conditions of this experiment each molecule absorbs a photon once

in a second, this result means that the average lifetime of the bleached state is 5×10^{-4} second.
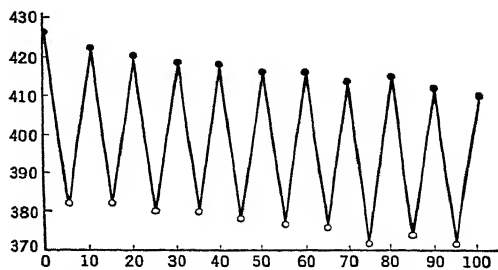
FIG. 1

These data relate to a very simple reaction — the dissociation of an iodine molecule into atoms:

$$I_2 \overset{h\nu}{\rightleftharpoons} I + I$$
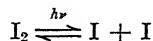
The "energetical yield" is up to 75 per cent, since I_2 can be dissociated with a quantum yield 1 by light $\sim$ 6000 A, corresponding to 48 Kcal per mole, whereas the chemical energy of two I atoms is 35 Kcal per mole. The back reaction — the recombination of I atoms — requires, under the conditions of the experiment, only 0.0005 second, because it occurs by each triple collision and does not need any activation energy.

To accumulate chemical energy in a process of this kind, it would be necessary to "trap" the free atoms, by a loose chemical binding or by adsorption (in the same way as atomic hydrogen is "frozen out" by liquid air).

An example of a reversible photochemical process in which the products are "trapped" and the back reaction therefore proceeds relatively slowly in the reversible reduction of dyestuffs.[20] The following is an example:

$$2 H^+ + 2 Fe^{2+} + \text{Thionine} \overset{h\nu}{\rightleftharpoons}$$
$$2 Fe^{3+} + \text{Leukothionine} \qquad (9)$$
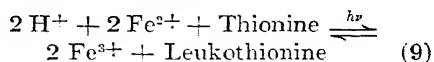
The normal potential of the system Thionine $\rightleftharpoons$ Leukothionine is about 0.5 volt; that of the system $Fe^{3+} \rightleftharpoons Fe^{2+}$, about 0.75 volt. In the dark, therefore, the ferric iron oxidizes the leuko dye, and the equilibrium (9) lies on the "left" side. Illumination accelerates the reduction of the dyestuff, the equilibrium is shifted "to the right," and the solution is decolorized.

The relative slowness of this back reaction as compared with that of iodine is due to the fact that the first, unstable reduction product, the radical D^-, (D = dyestuff) formed by the electronic transfer reaction

$$D^* + Fe^{2+} \rightleftharpoons Fe^{3+} + D^- \qquad (10)$$
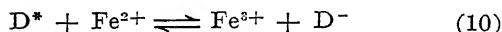
is "stabilized" by a second reaction:

$$2 D^- \rightleftharpoons D^{--} + D \qquad (11)$$
$$D^{--} + 2 H^+ \rightleftharpoons DH_2$$
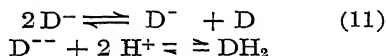
giving the leuko-ion D^{--} (or the neutral leuko dyestuff DH_2) which is a relatively stable compound.

How much of the light energy is converted into chemical energy in the illuminated dyestuff-iron salt system remains to be determined.

We have found some indications that a comparatively high efficiency of conversion can be achieved by means of chlorophyll. Chlorophyll solutions in methyl alcohol form with iron salts a reversible oxidation-reduction system

$$\text{Chlorophyll} + Fe^{3+} \rightleftharpoons \text{Oxidized}$$
$$\text{chlorophyll} + Fe^{2+} \qquad (12)$$
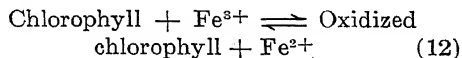
which is in a certain sense "reciprocal" to the thionine system. Chlorophyll is reversibly *oxidized* by means of Fe^{3+}, whereas thionine is reversibly *reduced* by Fe^{2+}. Some experiments — which are, however, of a preliminary character — point to-

* D* means excited dyestuff.

ward the possibility of substituting for Fe^{3+}, in (12), substances with a less positive potential, thus improving considerably the utilization of light energy. It is a tempting idea that chlorophyll, associated in nature with the great energy-converting process of photosynthesis, may have a capacity of converting light energy into potential chemical energy in other reactions as well.

In the "irreversible" energy-accumulating light reactions, the two problems essential for their practical use are:

(*a*) Sufficiently high energy yield.

(*b*) A product whose energy can be easily utilized.

In dealing with "reversible" endothermal photoreactions, the corresponding two problems are:

(*a*) A high energy yield.

(*b*) Utilization of the back reaction.

It is obviously useless to allow the back reaction to proceed in the ordinary thermal way, since this would amount to an indirect conversion of light into heat — which can be done directly. The light energy ought to be trapped, either by "stabilizing" the "activated" state or by "canalizing" the return of the sytem into the original state so as to make it produce electric current. We come in this way to the problem of potentials created by illumination of colored solutions. Holst[18] recently made some experiments on the electromotive forces produced by the illumination of the diazosulfite-methylene blue system.[8] Numerous observations exist on less exactly defined systems used in so-called photovoltaic cells ("Becquerel effect").

It would be interesting to develop these investigations further, e.g., to apply them to systems containing ferro-ferrisalt mixtures, as well as to chlorophyll solutions.

REFERENCES

1. A. HELMHOLTZ, "Erhaltung der Kraft," 1847, p. 25.
2. E. WARBURG, *Verhandl. deut. physik. Ges.*, 1907, 757.
3. F. WEIGERT, "Die chemischen Wirkungen des Lichts," Stuttgart, 1911.
4. A. EINSTEIN, *Ann. Physik*, 37, 832 (1912).
5. N. R. DHAR, "The Chemical Action of Light," Blackie and Son, 1931.
6. J. WEISS, *Nature*, 136, 794 (1935); R. M. POTTERILL, O. J. WALKER, and J. WEISS, *Proc. Roy. Soc.* (A), 156, 561 (1936).
7. J. WEISS and D. PORRET, *Nature*, 139, 101S (1937).
7a. J. M. BLAIR and P. A. LEIGHTON, *J. Opt. Soc. Am.*, 24, 1185 (1934).
8. E. WARBURG, *Berl. Akad. Ber.*, 1912, p. 216, 1914, p. 872; *Z. Elektrochem.*, 1921, 133.
9. O. WARBURG and E. WEGELEK, *Z. physik. Chem.*, 102, 248 (1922); *Naturwissenschaften*, 13, 985 (1925).
10. W. M. MANNING, C. JUDAY, and M. WOLF, *J. Am. Chem. Soc.*, 60, 274 (1938); W. M. MANNING, T. F. STAUFFER, B. M. DUGGAR, and F. DANIELS, *ibid.*, 266.
11. Unpublished results.
12. H. A. SPOEHR, "Photosynthesis," 1926, p. 336; BOYSEN-YENSEN, "Stoff Production der Pflanzen," 1932; BOSE, "Physiology of Photosynthesis," 1924.
13. R. EMERSON and W. ARNOLD, *J. Gen. Physiol.*, 15, 391 (1931), 16, 191 (1932); H. GAFFRON and K. WOHL, *Naturwissenschaften*, 24, 81 (1936); J. WEISS, *J. Gen. Physiol.*, 20, 501 (1937); K. WOHL, *Z physik. Chem.*, 37, 105 (1937).
14. *J. Chem. Phys.*, 6, 861 (1938).
15. G. SCHEIBE, *Kolloid Z.*, 82, 1 (1938); *Naturwissenschaften*, 25, 795 (1937).
16. H. BEUTLER, and E. RABINOWITCH, *Z. physik. Chem.* (B), 6, 233 (1930).
17. A. COEHN and WASSILJEWA, *Ber.*, 42, 2183 (1903); A. COEHN and M. BECKER, *ibid.*, 43, 880 (1910).
18. G. HOLST, *Z. physik. Chem.*, 163, 1 (1934), 175, 39 (1936), 178, 282 (1937).
19. E. RABINOWITCH and H. L. LEHMANN, *Trans. Faraday Soc.*, 31, 683, (1935); E. RABINOWITCH, and W. C. WOOD, *J. Chem. Physics*, 4, 497 (1936); *Trans. Faraday Soc.*, 32, 547, 816, 907 (1936); E. RABINOWITCH, and J. WEISS, *Nature*, 138, 1098 (1936); *Proc. Roy. Soc.* (A), 162, 251 (1937); D. PORRET and E. RABINOWITCH, *Nature*, 180, 321 (1937).
20. J. WEISS and M. FISCHGOLD, *Z. physik. Chem.* (B), 32, 135 (1936); 32, 1331 (1936). E. RABINOWITCH and J. WEISS, unpublished results.

SOME BAND SPECTRA IN EMISSION AT ATMOSPHERIC PRESSURE AND ORDINARY TEMPERATURE

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Emission spectra in nitrogen have been photographed using as a source of excitation an apparatus commonly known as as ozonizer. This apparatus consisted of two cylindrical glass dielectrics separated by a few millimeters of annular gas space, the outer surface of the outer cylinder and the inner surface of the inner cylinder having a metallic coating. When high alternating potentials of ordinary frequencies are applied to such a condenser, a discharge occurs in the gas space and the gas is feebly luminescent. Though the absolute luminosity is low, it is possible under such conditions to excite spectral emission in a gas which is held at atmospheric pressure and at the same time at room temperature. It is believed that such an apparatus may possess some advantages as a source of band-spectra excitation.

Working with such an apparatus with nitrogen, the oxygen content of which had been reduced by vaporizing metallic sodium in the gas, bands of the intersystem transition $A\,(^3\Sigma_u^+) \longrightarrow X(^1\Sigma_g^+)$ have been photographed under sufficient resolution to show clearly the rotational structure. Within the accuracy of measurement, which was rather low because of wide slit and serious temperature variation in the spectrograph room during the seven- to eight-hour exposure, the rotational structure is in agreement with that calculated from the rotational constants of the two levels which are known from measurements in other nitrogen bands. Hitherto these bands, involving the metastable triplet level of nitrogen, have been observed only at low pressures, although Kaplan[1] has recently observed them at as high as 10 mm pressure. It is of interest that in the present work they have been observed at atmospheric pressure.

The difference in character of the discharge in an apparatus such as described above and that in a high-tension low-current gas arc, both being at atmospheric pressure, is illustrated by the emission observed in oxygen. In the high-tension arc almost the entire emission consists of the well-known oxygen bands first studied by Runge[2] while in the ozonizer the only emission of prominence consists of the second positive group of nitrogen arising from the small amount of nitrogen impurity in the oxygen.

REFERENCES

1. *Nature*, April 9, 1938.
2. *Physica*, 1, 254 (1921).

SPECTROSCOPIC PLATES AND THEIR SENSITIZATION

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At earlier sessions of the spectroscopic conferences held at the Massachusetts Institute of Technology, special photographic plates for spectroscopy and astronomy have been described in detail. Some further developments can be announced, but it may be of interest first to review the subject of optical sensitization. It is fundamentally connected with spectral absorption and presents problems in this field.

The necessary condition for sensitization of a photographic emulsion to radiation which is not absorbed by the silver halide is, of course, extension of the spectral absorption to include the desired region. Because of technical difficulties, it has only recently been possible to secure adequate data correlating the spectral absorption and spectral sensitivity of emulsions. The difference between the wavelengths of absorption maxima of sensitizing dyes in solution and the maxima of sensitization has caused some uncertainty as to the mechanism of the process. In recent work, the results of which have been published in the *Journal of Chemical Physics*,[1] an attempt has been made to answer some of the questions concerned with this problem.

By means of an automatic spectrophotometer of the type developed at the Massachusetts Institute of Technology, it is possible to measure the spectral absorption of a photographic emulsion on a plate or film support. Blackening of the silver halide and bleaching of the sensitizing dyes, which make measurements on the ordinary type of spectrophotometer very uncertain, are reduced to a minimum by the rapid operation and the illumination of the sample with dispersed light. The intergrating sphere arrangement, with some modification of the commercial model, has proved satisfactory for diffusing systems like an photographic emulsion.

Spectral sensitivity was determined by the monochromatic sensitometer designed by Jones and Sandvik. Fig. 1 shows the curves of absorption and sensitivity for a strong panchromatic sensitization in a fast emulsion. The correspondence of the maxima in the curves is obviously very good. Similar data are available for a number of dyes and dye combinations, with satisfactory agreement in all cases. It should be noted that absorption is nearly complete for the shorter wavelengths. These data apply to a coating of normal thickness, so that for this region a silver halide emulsion loses little available energy by transmission. The absorption for wavelengths longer than about $450\ \mu$ might be considerably increased, but so far the possible gain in sensitivity by this means is subject to other limitations.

Fig. 2 shows the effect of increasing the concentration of sensitizing dye in an

emulsion. There is a definite optimum concentration, beyond which speed and contrast both decrease rapidly for all wave-lengths, i.e., both the regions of natural sensitivity and those of optical sensitiza-tion. The optimum concentration is found to be the maximum at which adsorption of the dyes from solution is practically
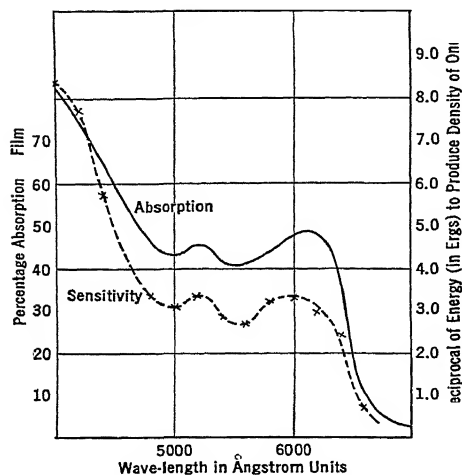
FIG. 1

complete, but the decrease in sensitivity beyond this point cannot be explained by filter action of unadsorbed dye. For three dyes studied, the surface concentration at the optimum was found to have a constant value independent of the photographic emulsion used. It appeared to be the right order of magnitude for a monomolec-ular layer, with the dye molecules lying flat on the surface. For most infrared sensitizers, the optimum concentration is a much lower value, limited in part by fog, but in any case far below the amount necessary to give reasonably com-plete absorption. The maximum optical sensitization produced by a given dye is usually determined not only by absorption,

but even more by the efficiency of energy transfer from the dye to the silver halide. At the best, as in the case just illustrated, the quantum efficiency does not vary greatly with wavelength, but for many other dyes it drops to values approaching zero. It is perhaps not generally realized that some dyes from practically all the main chemical classes are adsorbed to silver halides. However, if one were to choose ten dyes at random from all those which may be adsorbed, probably nine of these would affect sensitivity principally by decreasing it for the spectral region absorbed by the silver halide itself, and all would show this effect to a measur-able degree. The available evidence leads us to the conclusion that energy absorbed by the dye is transferred to the silver halide by some process which may be loosely described as analogous to collision of the second kind. After this, the energy is utilized to form the latent image in the same way as if it had been absorbed by the silver halide itself. Therefore, although perhaps half of the dyes adsorbed by
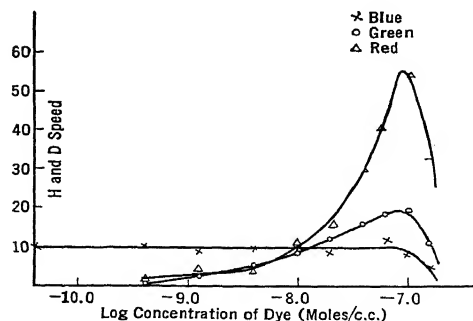
FIG. 2

silver halide produce detectable optical sensitization, most of them work against the handicap of general desensitization; add to this the variation in the efficiency of energy transfer, and the optical sensiti-

zation can, and does, show enormous differences when different dyes are used.

The most generally used sensitizers are of the cyanine group. The chemistry of these compounds is outside the field of this paper, but it is pertinent that they furnish some of the best data available connecting structure and spectral absorption. Fig. 3 shows the structures and absorption curves for some cyanine dyes produced

ever, it is necessary to be cautious in extrapolating data from absorption in organic solvents to those shown in optical sensitization of photographic emulsions. The region of sensitization is controlled by the absorption of the dyed silver grains, which generally is different in the shape of the absorption curve and location of the maximum from that of the solution of the dye in organic solvents. It has been found
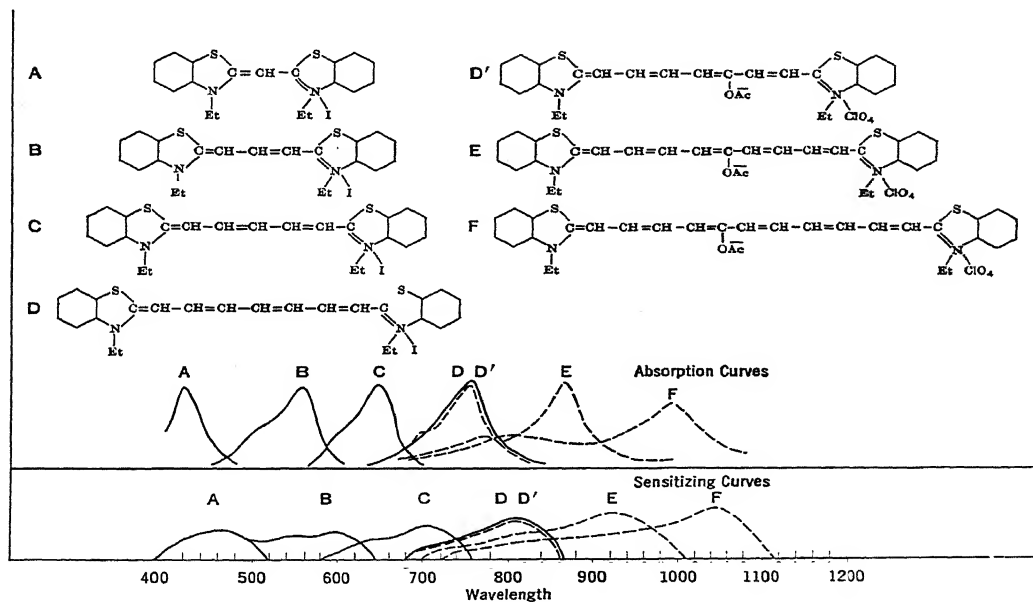
Fig. 3

from benzothiazol. This illustrates in the first place the relation between the wavelength of the absorption maximum and the length of the conjugated chain linking the nitrogen atoms. The molecular absorption coefficients of these dyes at the wavelengths of maximum absorption are of the order of 10^8; something of this order is necessary, so that a monomolecular layer of dye on the grains may absorb enough energy to produce good sensitization. How-

that the absorption of cyanine dyes is capable of considerable change with environment and concentration, adsorption to silver halide being only one of the conditions under which it may differ from the form taken in solution. These changes have been studied independently by Scheibe and his students at Munich,[2] and at the Kodak Research Laboratories.

Fig. 4 illustrates the results for a dye of the thiacarbocyanine class. The dye in

methanol (curve I) is almost certainly in true solution, and the absorption is believed to represent the monomolecular form, probably considerably ionized. In water (curve II) it is a colloidal electrolyte at the concentration illustrated; it is strongly ionized into halide and dye ions,

FIG. 4

the latter probably aggregated. If to the water solution is added a sufficient concentration of halide, the dye will be salted out; short of this stage, there is probably increased aggregation. This, however, is

FIG. 5

not merely a random coalescence to larger colloidal particles, but is associated with a definite new structure, producing a new absorption band (curve III). Direct evidence for this view is available for diethyl 2, 2'-cyanine, since Jelley[3] has found that, at high concentration, this dye aggregates in a form which he calls nematic crystals, having a space lattice extending along one dimension only. These are associated with a new absorption band of extraordinary sharpness, comparable with those of rare-earth solutions.

Fig. 5 shows the data for silver bromide dyed with the same thiacarbocyanine dye employed for Fig. 4. The absorption band appearing in aqueous bromide solutions is

FIG. 6

seen in emulsion (curve 2), in emulsion grains separated by centrifuging (curve 3), and in silver bromide dyed from aqueous solution in the absence of gelatin (curve 5). Silver bromide dyed by a methanol solution, however, shows an absorption band (curve 4) not much different from that of the methanol solution.

Fig. 6 shows wedge spectrograms of emulsion sensitized at low and at optimum concentrations of the dye. At the optimum concentration, the sensitization obviously corresponds to the absorption curve illustrated in curves 2, 3, and 5 of Fig. 6. At a low concentration, the dye is apparently in molecular dispersion and the spectrogram corresponds to curve 4. The data are presented in this form because of the difficulty of measuring the weak absorption corresponding to the low concentration.

From the theoretical standpoint, one of the most important points is that it is possible, at least in some cases, to obtain from the solution of the dye alone the same absorption as that of the dyed silver halide for the longer wavelengths. This indicates that the energy of absorption is not the factor modifying the spectral absorption of the dye. It is our opinion that the new absorption is characteristic of a new molecular configuration, which may be a one- or two-dimensional crystal lattice. Scheibe, however, ascribes it to an aggregate of definite molecular weight, and presents some distribution data to show that the absorption bands of pinacyanol in water solution correspond to aggregates of two and ten molecules. Aqueous solutions normally give broader absorption bands, as just shown. Combinations of dyes may show a marked mutual influence on absorption and sensitization. In general, the effect of a combination of dyes is less than the sum of their individual sensitizations, but in a few cases the sensitizing action of one dye is improved by the presence of another.

These data seem to us sufficient to indicate that photographic sensitization is a normal type of sensitization of a photochemical process, in which energy absorbed by one part of the system is transferred to another in which the actual reaction takes place.

While the mechanism of sensitization appears to be at least consistent with views on other photochemical processes, progress in its application is largely a matter of empirical experiment. This is carried on continuously, and results are applied as they become available. In general, improvements in sensitization of spectroscopic plates fall within the general scheme first set up, in which there is a number of basic emulsions, each of which can be supplied with a series of different spectral sensitizations. The emulsions and sensitizations are described in full in the booklet " Photographic Plates for Use in Spectroscopy and Astronomy " published by the Eastman Kodak Company. A number of improvements have been made since the last edition of this booklet, which will be described briefly. The most important is a general increase in the speed of all plates sensitized for the visible region and near infrared, up to and including the R type. This does not apply to the far infrared sensitizations (P, M, Q, and Z) nor to unsensitized emulsion (O). The increase is of the same order for all wavelengths, including the blue and violet, in distinction to hypersensitizing, which favors the region of optical sensitization; there is no change in grain size or contrast. The extent varies with the emulsion type and sensitization.

A new ultraviolet sensitizing is available, which gives a definite improvement over the old type in the region around 2000 A. It is a non-crystalline material, which affords possibility of higher resolving power than has been obtainable with ultraviolet sensitized spectroscopic plates.

For those interested in plates of very high resolving power, a new type V emulsion is now available with a speed considerably above that of the present standard. It may, unlike the old type V, be sensitized for the near infrared, types U, K, R, N, and P having been prepared. The distribution of sensitivity is different at the blue end, as shown in Fig. 7, which gives curves of spectral sensitivity for the standard and new type V-C. Graininess and contrast are very nearly the same as those of the standard.

Two of the sensitizations have been modified and a new type introduced. The new N type available in types I, II, and

Va emulsions is appreciably faster and gives more uniform sensitization from 7000 to 8500 A than formerly.

A new U-type sensitizing has been developed which has its maximum at 7200 A
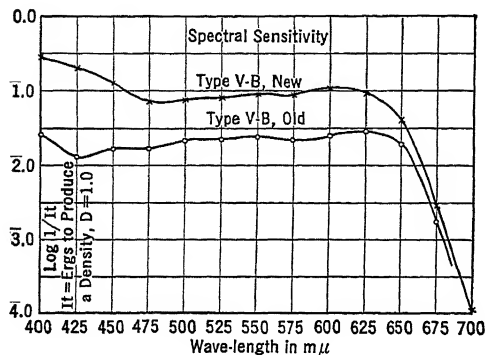
Fig. 7

instead of at 7000 A as given by the original sensitization. It is superior to the original sensitization throughout the range of the latter and extends to longer wavelengths.

There have been supplied to several observatories plates specially sensitized for the region of the H-α line. One of these, which is continuing to be called the H-α sensitization, has a sharp maximum at 650 μ; it is supplied only in types I and II emulsions. The other, which it is proposed to call E sensitizing, has a broader maximum at the same point, and the highest general sensitivity to the red which has been secured to date; it is available in all emulsion types. This has been used by Professor W. H. Wright of Lick Observatory for photography of stars in nebulae. It appears possible to produce other sensitizations having strong maxima in particular regions. These are typical investigations at present in progress in the continuous effort to improve the spectroscopic plates.

REFERENCES

1. LEERMAKERS, CARROLL, and STAUD, *J. Chem. Phys.*, 5, 878 (1937); LEERMAKERS, *ibid.*, 5, 889 (1937); LEERMAKERS, CARROLL, and STAUD, *ibid.*, 5, 893 (1937).
2. *Kolloid Z.*, 82, 1 (1938).
3. *Nature*, 139, 631 (1937).

THE PHOTOGRAPHIC LATENT IMAGE FROM THE STANDPOINT OF THE MODERN THEORY OF SOLIDS

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INTRODUCTION

The photographic latent image has been an outstanding problem since the beginning of photography now more than a hundred years ago. A great deal of experimental work has been done and many theories have been proposed to account for the nature and formation of the latent image. Recently this problem has been considered in the light of the modern atomic theories of solids as developed along the lines of the new quantum mechanics. First attempts in this direction proved very promising, and it now appears that these newer methods will lead to a complete understanding of this problem. The purpose of this paper is to outline the picture of latent-image formation in its most recent development along these lines, and to present experimental results which support this theory.

Prior to the application of the methods of quantum mechanics to the latent-image problem, theories relating to this subject had seemed to reach an impasse. The theories correlated the general facts about the latent-image process but said very little about the underlying mechanism. The theory of latent-image formation which for some time has been most generally accepted and which seems to sum up the facts better than any other is the so-called concentration speck theory proposed by Sheppard, Trivelli, and Loveland[1] in 1925. According to this theory, the latent image itself is recognized as a small number of neutral Ag atoms adhered together about a sensitivity speck. Experiment has shown that these sensitivity specks exist and that they consist of tiny nuclei of foreign atoms on the surface of the AgBr grain. It is assumed that light is absorbed over the entire area of the photographic grain, but that the Ag atoms formed by photochemical action are located at discrete points adjacent to the sensitivity specks. This theory attributes to the speck only the function of concentrating the Ag atoms reduced by the light. However, it says little about the mechanism whereby light absorbed over the surface of the entire grain can manifest itself at discrete points. In a certain sense the concentration speck theory can be compared to the thermodynamics treatment of a problem. It correlates the experimental facts without much attempt to describe the mechanism by which the process takes place. The treatment of this problem in accordance with the modern theories of solids appears to be supplying the explanation of the mechanism for the process.

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The most recent contribution to the subject of latent-image theory is the work by Gurney and Mott.[2] The introduction by these workers of the concept of electrolytic transport of $+$Ag ions as an accessory process of latent-image formation is thought to be a significant advance. This new concept appears to be the missing link in the mechanism by which light absorbed over the entire surface of a AgBr crystal can lead to the formation of clumps of Ag atoms coagulated together at discrete points. A brief description of the theory of latent-image formation as it has been modified by the recent work of Gurney and Mott will now be given.

THEORY OF LATENT-IMAGE FORMATION

To describe the theory of latent-image formation, we take as the starting point the energy diagram of a AgBr crystal as derived from quantum mechanics considerations. An idealized energy diagram of this type is shown in Fig. 1. As is
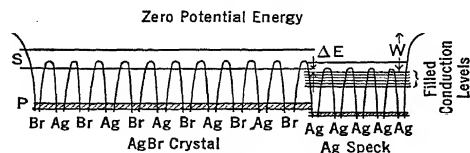
FIG. 1

known, the electronic energy spectrum of an insulating crystal like AgBr includes bands of allowed levels separated by disallowed zones. For purposes of discussing the latent-image problem, only two of the allowed bands need be considered. One of these is an upper S band which is normally empty and which is referred to as the conduction band, and the other is a lower P band which is normally completely filled with electrons. Upon exposure of a AgBr crystal to light absorbed in the long-wavelength end of the characteristic absorp-

tion band, the crystal becomes conducting. This property is known as photoconductance and, on the basis of the present picture, results from the transference of electrons by light from the lower P band of levels to the upper S conduction band. Electrons in this upper conduction band behave exactly like free electrons in a metal and give rise to conductivity.

Primary Process. In common with a number of previous workers, Gurney and Mott have assumed in their theory that the initial process of latent-image formation is to be identified with the photoconductance effect. There is good experimental evidence to show that these two processes are the same, chief of which is their agreement in spectral sensitivity.[3] As a result of this initial action of light, it is assumed that there is created within the single-crystal photographic grain a sort of atmosphere of free electrons. These electrons may be expected to move about in the crystal, and to be reflected at the boundaries. However, there is always a certain probability that the electrons so released may become stuck in localized levels[4] existing around irregularities in the crystal, or that they may fall back into the original levels (levels of the parent bromine atoms) from which they came. On this account this gas of electrons may not be expected to persist indefinitely in the crystal.

To explain the next step in the latent-image process, the so-called sensitivity specks are brought into account. Work by Svedberg,[5] Toy,[6] Clark,[7] Sheppard, Trivelli, Loveland, and Wightman,[8] and others showed that foreign specks exist on the grains prior to exposure and that these specks play an important role in latent-image formation. Work by Sheppard,[9] Clark,[10] and others showed further that these specks of foreign material consist

largely of Ag_2S. There is also evidence[10] to indicate that there is colloidal Ag in combination with the Ag_2S. In line with the most generally accepted theories of latent-image formation today, Gurney and Mott identify the latent-image with metallic silver and assume that the function of the sensitivity specks is to act as centers for the nucleation of the latent-image silver during exposure to light. They have proposed the following new concept to explain how the sensitivity specks act to accomplish this.

Secondary Process. As stated above, it must be supposed that, during exposure to light, there is created within the photographic grain a sort of gas of free electrons. Gurney and Mott assume that some of these electrons, in their excursions through the crystal, will come in contact with the sensitivity specks located on the surface of the grain and become trapped there. The way in which this trapping is supposed to occur may be seen by reference to Fig. 1. The energy levels of a Ag speck are shown adjacent to those of AgBr. If the highest occupied level of the conduction band of Ag falls below the conduction band of AgBr as shown here, then an electron will fall down the potential hill and become trapped.* Such a mechanism would explain the trapping of electrons when Ag is present in the sensitivity specks. If the specks consist originally of Ag_2S alone, then the same mechanism for trapping is to be assumed. The only condition that need be fulfilled is that the conduction band of Ag_2S fall below that of AgBr.

When the electrons become trapped on the sensitivity specks in the manner just outlined, these specks acquire a negative charge. The charged speck is then supposed to act by electrostatic attraction to draw to itself interstitial $+Ag$ ions, which have been dislodged by heat motion from their regular lattice positions in the crystal. These ions diffuse to the specks, and upon reaching the negatively charged specks, neutralize the excess electrons there to form Ag atoms. The metallic clumps so formed are assumed to be the nuclei active in inducing development of a grain. The source of $+Ag$ ions for building up the Ag clumps, as just described, is the same as that invoked to explain ionic conductivity in the Ag-halide crystals. It has been shown experimentally[13] that the ionic conductivity in the AgBr crystal is to be attributed to the movement of $+Ag$ ions. Frenkel[14] has given a theoretical model to explain how this comes about, and further theoretical work has been done by Jost.[15] According to this picture, at any temperature, T, a certain number of $+Ag$ ions will be dislodged by heat motion from their regular lattice positions and removed to interlattice positions. Under the combined influence of heat motion and an electric field, these $+Ag$ ions can diffuse through the crystal, the supply of such ions being dependent upon the temperature, and their rate of migration dependent upon both temperature and the magnitude of the electric field.

<center>EXPERIMENTAL PART</center>

Effect of Low Temperature. From the foregoing theoretical picture, certain predictions can be made about the effect of low temperature on the photographic process. The primary process of latent-image formation, consisting of internal release of electrons by light absorption and the subsequent movement of these electrons through the crystal, is believed to be little

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*Experimental evidence that electrons can be trapped by colloidal specks of metal as suggested here has been obtained by Glaser and Lehfeldt[11] for KCl crystals and by Lehfeldt[12] for AgBr crystals.

affected by low temperature. This belief is based on experiments on photoconductivity carried out by Lehfeldt[12] in which no drop in photoelectron yield was found down to the temperatures of liquid air. The secondary process of latent-image formation, consisting of electrolytic transport of $+$Ag ions, is, however, expected to be critically dependent upon temperature. At the temperature of liquid air, mobility of the $+$Ag ions, if not completely eliminated, should at least be very materially decreased. The following experiments were carried out to determine what effect this would have on the photographic process. Their interpretation will be reserved until after presentation of the results.

The first experiment to be described (Fig. 2a) illustrates the effect of low temperature ($-186°$ C) on the sensitivity of the emulsion used in these tests. The exposures in this experiment were made through a neutral density step wedge placed in front of the film. For temperature control, the emulsion was immersed in liquid air by inserting the film in a metal guide placed vertically against the interior wall of a transparent Dewar flask. The 157-candle-power light source used in the exposures was placed at a distance of 4 meters from the film, and the total time of the exposure was 160 seconds. The characteristic curves (density vs. log exposure) made at room temperature ($20°$ C) and at liquid-air temperature ($-186°$ C) are shown in Fig. 2a. It will be noted that there is a very large drop in sensitivity of the emulsion as a result of the lowered temperature.

The other experiments shown in Fig. 2 pertain to interrupted exposures made at liquid-air temperature. These experiments consisted of two series of intermittent exposure (A) and (B) made at liquid-air temperature ($-186°$ C). In both series

(A) and (B) the emulsion was exposed in the same way. The only difference between the two series was in the treatment received by the emulsion between flashes. In the (A) series, the emulsion was warmed up to $20°$ C for a brief time during the dark period following each flash, and then lowered again to $-186°$ C before the succeeding flash was applied; in the (B) series the emulsion was maintained at $-186°$ C throughout the intervening dark period. The length of the dark period between flashes was the same for series (A) and (B), amounting in both to 2 minutes.

The (B) curves of Fig. 2 show that there is no noticeable effect from interrupting the exposure made at liquid-air temperature, providing the low temperature is maintained during the intervening dark periods. The (A) curves, on the other hand, show that the same procedure produces a marked effect if the emulsion is warmed up between flashes. Breaking the exposure into two 80-second flashes and giving one warm-up period (Fig. 2b) materially increased the resulting photographic effect. Breaking the exposure into four 40-second flashes (Fig. 2c) and warming up between flashes still further enhanced the photographic effect, and breaking the exposure into eight 20-second flashes (Fig. 2d) with warm-up periods brought the sensitivity up to a value comparable with the sensitivity at $20°$ C.

These experiments show that some action vital to the latent-image process takes place during the warm-up periods between flashes. According to the Gurney-Mott picture, this action consists of the movement of $+$Ag ions to the charged sensitivity specks. The manner in which the warm-up periods act to increase the sensitivity of an emulsion is thought to be interpretable in the following manner: Let it be supposed that the first flash leads to the trapping of several
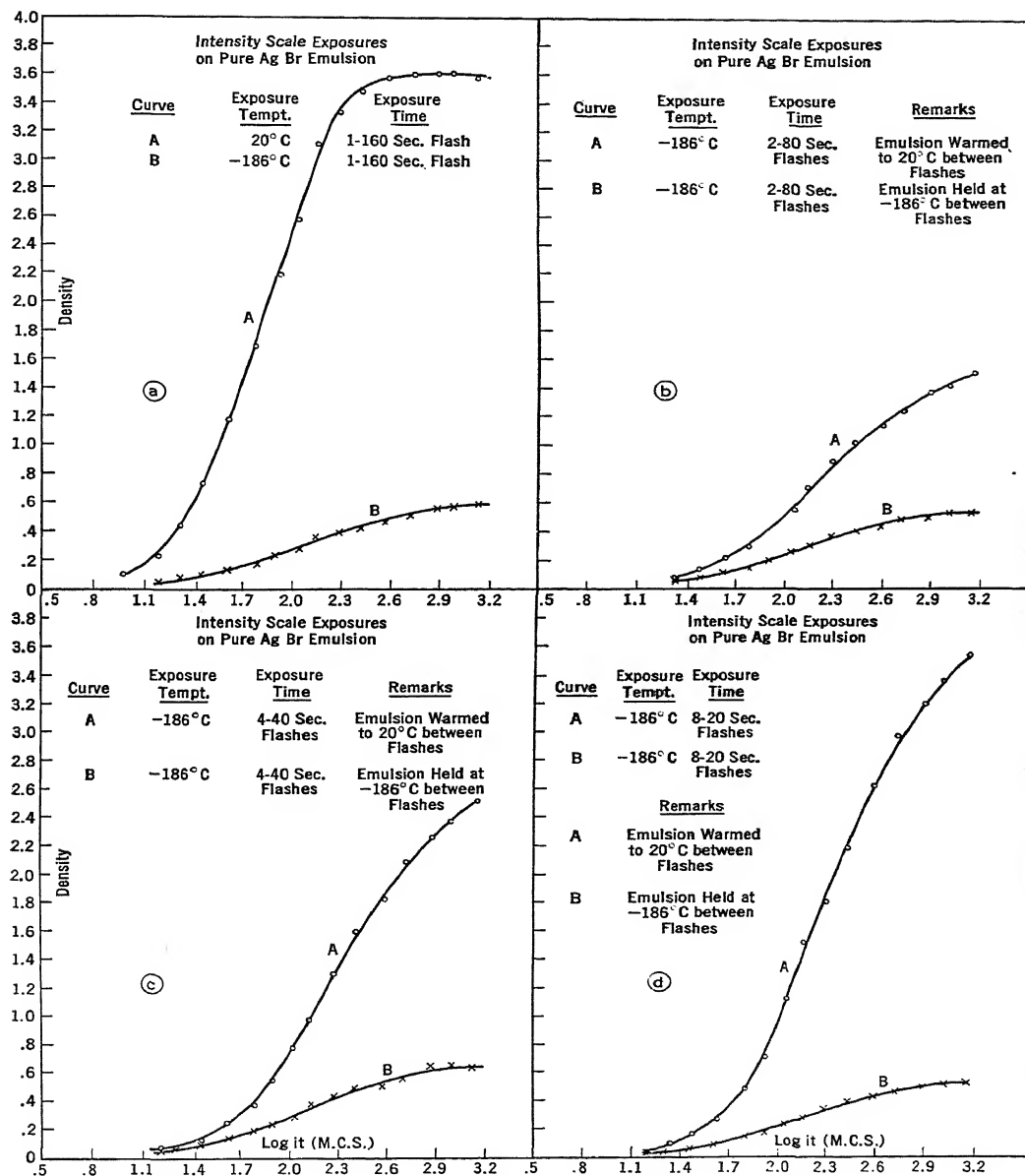
Fig. 2

electrons on a sensitivity speck; then, upon warming up the emulsion, $+$Ag ions can move up to the speck and neutralize these electrons. A further flash exposure at low temperature will now add several more electrons to the speck and, upon warming up again, further $+$Ag ions will diffuse to the speck. As a given exposure is broken into more and more flashes, this process is repeated over and over, and since the greater the number of flashes, the smaller the negative charge that need be added to the speck at each flash, the less is the un-neutralized charge placed on the speck at each flash. Since, for smaller unneutralized charges, fewer electrons are repelled and thereby lost for the latent-image process, the photographic effect should increase in proportion to the number of flashes (with intervening warm-up periods) into which the total exposure is broken.

The foregoing experimental results are considered as affording strong evidence in support of the Gurney-Mott assumption that electrolytic transport of $+$Ag ions constitutes the secondary process of latent-image formation.

Herschel Effect. The results now to be reported are thought to give added evidence that there is a secondary process of latent-image formation and that this process consists of an electrolytic movement of $+$Ag ions. These experiments pertain to the Herschel effect, which consists of the erasure by infrared light of the forward action of a previous exposure to white light. These experiments were also made under conditions of varied temperature.

The results of the Herschel exposures are shown in Fig. 3. In these diagrams, the straight horizontal line represents the density obtained by a primary flash exposure to white light. The points with circles represent the diminished density values obtained upon subsequent exposure to infrared light superposed on the white-light exposure. In these experiments, the primary exposures to white light were adjusted so as to give approximately the same density at 20° C and —186° C. The infrared exposures were identical at the two temperatures. The infrared exposures were made through a neutral density step wedge to radiation from a 500-watt tungsten lamp, filtered by two No. 87 and one No. 25 Wratten filters, at a distance of 0.6 meter.

The curves of Fig. 3a show the normal Herschel effect for which both the white-light exposure and the subsequent infrared exposure were made at 20° C. The curves of Fig. 3b show the results when the white-light exposure was made at 20° C and the infrared Herschel exposure was applied after the emulsion had been taken down to —186° C in temperature. As may be seen, no Herschel effect was obtained here. The results of a third experiment are shown in Fig. 3c, in which the white-light exposure was made at —186° C and the Herschel exposure applied after the emulsion was warmed up to 20° C. It may be seen that a considerable Herschel effect was obtained again in this case. Identical results with those of Fig. 3a are not to be expected here, since the original densities from the white-light exposures in the two cases are thought to result from different grain size distributions. The last experiments of the series are shown in Fig. 3d corresponding to the case for which the white-light exposure and the subsequent infrared exposure were both made at —186° C. The lower curves correspond to the case in which the emulsion was maintained at —186° C during the interval between the two exposures, while the upper curves pertain to the case in which the emulsion was warmed up to 20° C between the white-light exposure and the infrared exposure.

The results on the Herschel effect find ready interpretation in the Gurney-Mott theory of latent-image formation. In order to see this, it is necessary to consider briefly the explanation of the Herschel effect on the basis of this theory. For this purpose let us consider a single grain which has received an exposure to white light. The light releases internal electrons, which,

the metallic speck, into the conduction band of the AgBr (see Fig. 1). Disintegration of the metallic speck follows by the diffusion away of the +Ag ions of the speck. By means of this analysis, it is thought that all the results of Fig. 3 can be explained satisfactorily. The normal Herschel effect at 20° C (Fig. 3a) results from the formation and disintegration of
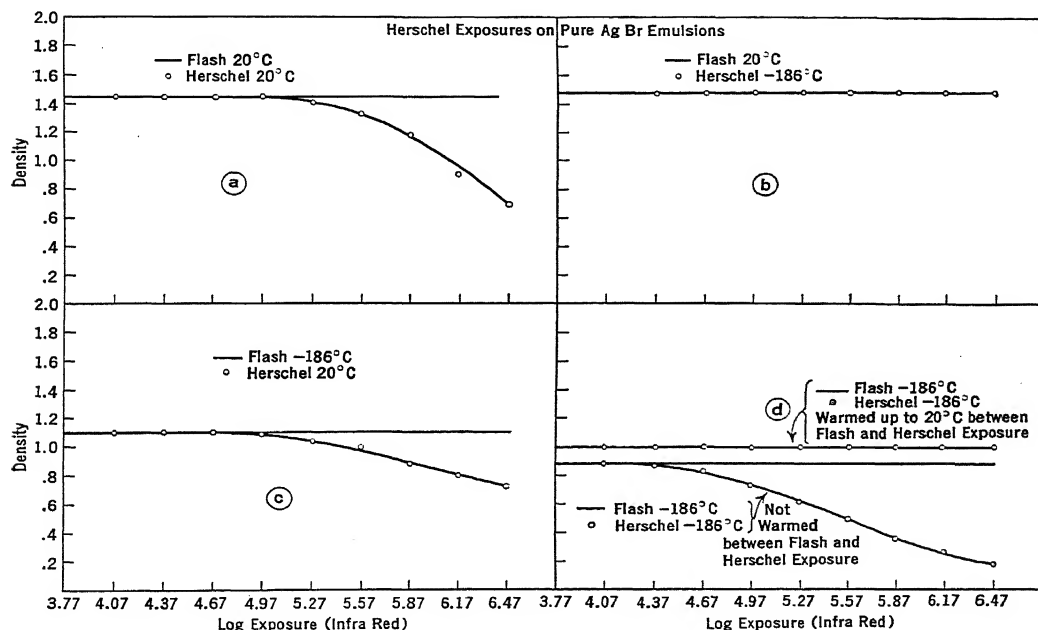
FIG. 3

in turn, become trapped on the sensitivity specks. If the crystal is at room temperature, it is supposed that +Ag ions diffuse to the negatively charged specks to form specks of metallic Ag around these sensitivity specks.* The Herschel exposure to infrared light is assumed to destroy this speck of metallic Ag, or at least to reduce its size. This comes about as a result of the ejection of electrons from filled levels of

the latent-image speck as just described. Consider now the case in which the white-light exposure is given at 20° C and the emulsion then lowered to −186° C for the Herschel exposure (Fig. 3b). On exposure to the infrared light at the low temperature,

* If the crystal is exposed at −186° C, it is thought that the electrons go to the sensitivity specks as usual, but that the +Ag ions cannot diffuse to the speck until the crystal is warmed up.

the electrons will be ejected from the levels of the metallic speck just as before, but now the $+$Ag ions cannot diffuse away at the low temperature. Thus, the electrons ejected will be attracted back again to the latent-image specks and the silver nuclei will remain intact after the infrared light stimulus is withdrawn. We consider next the case for which the white-light exposure was made at $-186°$ C and the Herschel exposure was made after the emulsion had been warmed up to 20° C. This case should correspond very closely to the one in which both exposures were made at 20° C, since warming up the emulsion for the Herschel exposure permits the completion of the formation of the latent image, which then is subject to destruction in the same way as that described for the normal case. It may be seen from Fig. 3c that a normal Herschel effect was obtained in this case.

The last experiment of the series is that in which both the white-light exposure and the Herschel exposure were applied at $-186°$ C. The lower curve (Fig. 3d), which shows a marked Herschel effect, corresponds to the case in which the emulsion was maintained at $-186°$ C between the two exposures, while the upper curve corresponds to that in which the emulsion was warmed up to 20° C between the exposures. The explanation of the two cases is thought to be as follows: In the case where the emulsion was maintained at the low temperature between exposures, the $+$Ag ions never diffused to the speck to complete the formation of the latent image. Upon subsequent exposure of the negatively charged specks to the infrared light, the electrons trapped on the specks were ejected and the potential latent image thereby erased. From the magnitude of the effect here, it would appear that the erasure of the photographic effect of the first exposure is more

complete under these conditions than if the latent image were completely formed. The experiment corresponding to the upper curve of Fig. 3d was in every way identical with the above one except that the emulsion was warmed up to room temperature between the white-light and infrared exposures. In this case, it is supposed that the warm-up period allows the diffusion of $+$Ag ions to take place and therefore the formation of the latent image to be completed. However, when the temperature is again lowered for the infrared exposure, conditions will be the same as for the experiment shown in Fig. 3b. The electrons can now be ejected from the speck, but the $+$Ag ions cannot follow, and therefore the speck is not destroyed.

Reciprocity Law Failure. The theory of latent-image formation advanced by Gurney and Mott offers a very plausible explanation of the reciprocity law failure at high intensity. At high light intensities it is supposed that the electrolytic movement of $+$Ag ions cannot keep pace with the movement of electrons to the sensitivity specks. The unneutralized negative charge resulting on the specks will then build up a repelling force for further electrons and thereby hold down the subsequent rate of trapping of electrons to the rate at which $+$Ag ions can reach the specks. As a consequence, many internally released electrons will be lost in this way for the latent-image process, resulting in an effective decrease in speed of the emulsion. This effect will obviously become more pronounced as the intensity increases and will therefore manifest itself as a loss of sensitivity with increased intensity level.

In order to investigate the prediction of the theory pertaining to the reciprocity law failure, some experiments were carried out at low temperature. The results of these experiments are shown in Fig. 4. The nor-

mal reciprocity curve at room temperature (20° C) is shown on the diagram. At this temperature, the curve exhibits a minimum at an intermediate intensity level known as optimal intensity. The rise of the curve at intensities above and below optimal shows that more exposure is required to produce a given density at these

high-intensity end. It thus appears that the high-intensity reciprocity law failure is also disappearing with lowered temperature. This is as it should be according to the Gurney-Mott theory. The loss of efficiency at high intensity is attributed to the sluggishness with which the +Ag ions diffuse to the charged specks. At suffi-
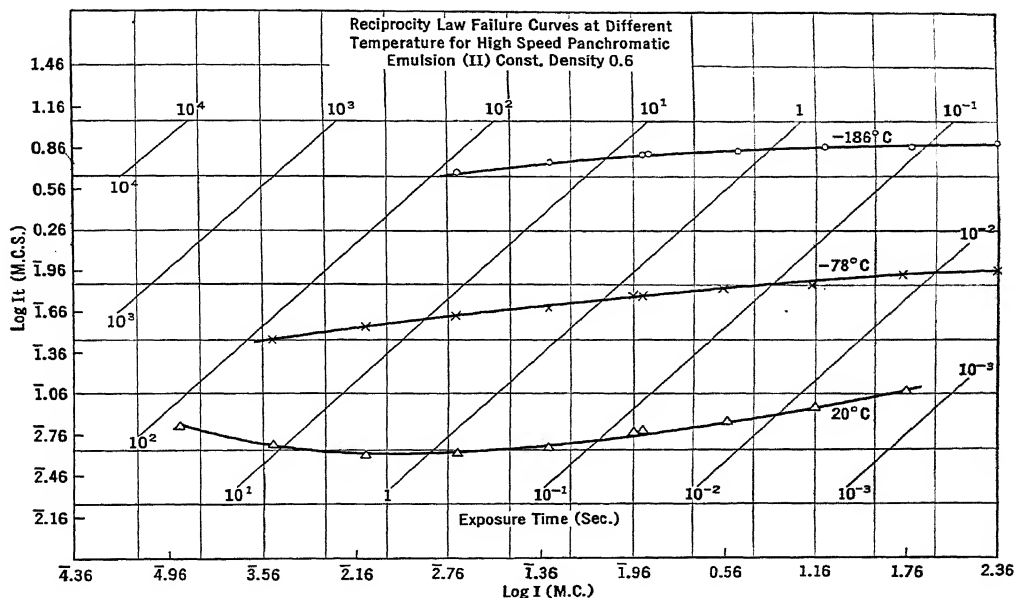
Fig. 4

intensity levels. The rise of the curve in these regions is termed the high- and low-intensity reciprocity law failures, respectively.

The curves of Fig. 4 show that the low-intensity reciprocity law failure diminishes rapidly with lowered temperature. At —78° C there is no indication of the upturn of the curve down to the lowest intensities reached. At the still lower temperature of —186° C the curve has become flatter throughout and there appears to be an increased tendency to flatness at the

ciently low temperature, the +Ag ions cannot reach the speck during the entire exposure period. When this condition is attained, the sensitivity should no longer be a function of the intensity level. It is obvious that either high intensity or low temperature can produce this effect, since either will act to slow up the +Ag ion diffusion rate relative to the rate at which electrons are trapped by the sensitivity speck.

The low-intensity reciprocity law failure is thought to be due to the thermal disintegration of the latent-image speck as it be-

gins to form and while it is still small. It is easy to believe that the stability of the speck would depend upon its size, since at larger sizes the Van der Waals force of cohesion might be expected to come into play to stabilize the speck. The above results at low temperature are in line with this explanation, since at lowered temperature the low-intensity reciprocity law failure disappears.

More direct evidence that the low-intensity reciprocity law failure is to be ascribed to a breaking up of the latent-image speck while it is still small is given by the curves of Fig. 5. In this figure are shown results
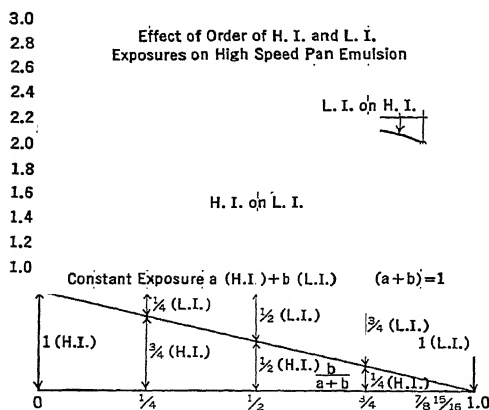
FIG. 5

obtained by a series of equal-energy mixture exposures made partly at high intensity (H.I.) and partly at low intensity (L.I.) as indicated by the diagram at the bottom of of the graph. The upper curve corresponds to exposures in which the H.I. was put on first and the L.I. second; the lower curve corresponds to exposures in which the L.I. was put on first and the H.I. second. The point farthest to the left on these curves corresponds to an all H.I. exposure; the point

farthest to the right corresponds to an all L.I. exposure. The difference in level of these two points represents, therefore, the reciprocity law failure between these two intensity levels. The points on each curve between these extreme limits correspond to mixture exposures of different proportions of low and high intensity, and the difference in the course of the two curves is attributable entirely to the difference in the order of the L.I. and H.I. exposures. It appears that, if a considerable proportion of the exposure is made at H.I. and is put on first, then the subsequent L.I. exposure is rendered just as efficient as the original H.I. part of the exposure.

The above results have been interpreted to mean that the latent-image speck of metallic silver becomes stable, and thereby ceases to regress only after it has reached a given size. When this stable stage is reached, it appears that the subsequent exposure can be applied at an intensity level as low as desired without loss of efficiency. If this interpretation is correct, then it must be concluded that the reciprocity law failure at low intensities is due to the disintegration of the latent-image speck as it begins to form and while it is still small.

The above experimental results have suggested that a pre-exposure to high-intensity light might be of considerable benefit to astronomers and spectroscopists in recording weak images of stars of spectral lines. For the emulsion shown in Fig. 5, it is possible to secure a gain of from two to four times in threshold speed by a pre-exposure of about ½ second at optimal intensity.

ACKNOWLEDGMENT

REFERENCES

1. S. E. SHEPPARD, A. P. H. TRIVELLI, and R. P. LOVELAND, *J. Franklin Inst.,* 200, 51 (1925).
2. R. W. GURNEY and N. F. MOTT, *Proc. Roy. Soc. London,* 164, 151 (1938).
3. F. C. TOY, *VII Intern. Congr. Phot., London,* p. 14, 1928. See also W. LEHFELDT, *Nachr. Ges. Wiss. Göttingen,* Math.–physik Klasse, 1, 171 (1935).
4. I. TAMM, *Physik. Z. Sowjetunion,* 1, 722 (1932).
5. T. SVEDBERG, *Phot. J.,* 62, 183 (1922).
6. F. C. TOY and W. CLARK, *Phil. Mag.,* 44, 352 (1922).
7. W. CLARK, *Phot. J.,* 48, 1, (1924).
8. S. E. SHEPPARD, A. P. H. TRIVELLI, and E. P. WIGHTMAN, *Phot. J.,* 67, 281 (1927); S. E. SHEPPARD, A. P. H. TRIVELLI, and R. P. LOVELAND, *J. Franklin Inst.,* 200, 51 (1925).
9. S. E. SHEPPARD, *Phot. J.,* 65, 1, (1925).
10. W. CLARK, *Brit. J. Phot.,* 74, 227 (1927).
11. G. GLASER and W. LEHFELDT, *Nachr. Ges. Wiss. Göttingen,* Math.–physik Klasse, II, 91 (1936).
12. W. LEHFELDT, *ibid.,* 1, 171 (1935).
13. C. TUBANDT and S. EGGERT, *Z. anorg. Chem.,* 110, 196 (1920).
14. I. FRENKEL, *Z. Physik,* 35, 652 (1926).
15. W. JOST, *J. Chem. Phys.,* 1, 466 (1933).

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